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Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas

*Industrial Emissions Directive
2010/75/EU
(Integrated Pollution
Prevention and Control)*

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Abstract

The BREF entitled 'Refining of Mineral Oil and Gas' forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection, and the Commission, to draw up, review, and where necessary, update BAT reference documents as required by Article 13(1) of the Industrial Emissions Directive (2010/75/EU). This document is published by the European Commission pursuant to Article 13(6) of the Directive. This BREF for the refining of mineral oil and gas covers certain industrial activities specified in Section 1.2 of Annex I to Directive 2010/75/EU, namely the energy industries of the refining of mineral oil and gas sector.

In particular, this document covers the following refineries processes and activities:

- | | |
|--|--|
| - Alkylation | - Hydrogen production |
| - Base oil production | - Isomerisation |
| - Bitumen production | - Natural gas plants |
| - Catalytic cracking | - Polymerisation |
| - Catalytic reforming | - Primary distillation |
| - Coking | - Product treatments |
| - Cooling | - Storage and handling of refinery materials |
| - Desalting | - Visbreaking and other thermal conversions |
| - Combustion of refinery fuels for energy production | - Waste gas treatment |
| - Etherification | - Waste water treatment |
| - Gas separation | - Waste management. |
| - Hydrogen consuming processes | |

Important issues for the implementation of Directive 2010/75/EU in the refining of mineral oil and gas sector are the emissions to air of volatile organic substances, nitrogen oxides, sulphur oxides, hydrofluoric acid, ammonia, carbon monoxide, dioxins and furans, and dust; emissions to water of oils, benzene, suspended solids, COD, nitrogen, metals (lead, cadmium, nickel, mercury); energy efficiency; and the prevention of emissions to soil and groundwater. The BREF document contains seven chapters. Chapters 1 and 2 provide general information on the refining of mineral oil and gas industry and on the industrial processes and techniques used within this sector. Chapter 3 provides data and information concerning the environmental performance of installations in terms of current emissions, consumption of raw materials, water and energy, and generation of waste. Chapter 4 describes the techniques to prevent or reduce emissions from installations in the sector. In Chapter 5 the BAT conclusions, as defined in Article 3(12) of the Directive, are presented for the refining of mineral oil and gas industry. Chapters 6 and 7 are dedicated to emerging techniques as well as to concluding remarks and recommendations for future work in the sector, respectively.

Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas

Industrial Emissions Directive 2010/75/EU
Integrated Pollution Prevention and control

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This report was produced by the European Integrated Pollution Prevention and Control Bureau (EIPPCB) at the European Commission's Joint Research Centre – Institute for Prospective Technological Studies (IPTS) under the supervision of Serge Roudier (Head of the EIPPCB) and Luis Delgado Sancho (Head of the Sustainable Production and Consumption Unit).

The authors of this BREF were Pascal Barthe and Michel Chaugny.

This project report was drawn up in the framework of the implementation of the Industrial Emissions Directive (2010/75/EU) and is the result of the exchange of information provided for in Article 13 of the Directive.

Major contributors of information were:

- among industry, Concawe representing the European oil industry and EIGA (the European Industrial Gases Association);
- among environmental NGOs, the European Environmental Bureau (EEB);
- among EU Member States, Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, the Netherlands, Poland, Portugal, Slovakia, Spain, Sweden, and the United Kingdom.
- among non-EU EEA Member States, Norway.

The whole EIPPCB team provided contributions and peer reviewing; among others, Magdalini Topouzidou contributed to the work in the months before the final TWG meeting and Michele Canova finalised the report.

This document is one from the series of foreseen documents listed below (at the time of writing, not all documents have been drafted):

| Reference Document on Best Available Techniques | Code |
|--|-------------|
| Ceramic Manufacturing Industry | CER |
| Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector | CWW |
| Emissions from Storage | EFS |
| Energy Efficiency | ENE |
| Ferrous Metals Processing Industry | FMP |
| Food, Drink and Milk Industries | FDM |
| Industrial Cooling Systems | ICS |
| Intensive Rearing of Poultry and Pigs | IRPP |
| Iron and Steel Production | IS |
| Large Combustion Plants | LCP |
| Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers | LVIC-AAF |
| Large Volume Inorganic Chemicals – Solids and Others Industry | LVIC-S |
| Large Volume Organic Chemical Industry | LVOC |
| Management of Tailings and Waste-rock in Mining Activities | MTWR |
| Manufacture of Glass | GLS |
| Manufacture of Organic Fine Chemicals | OFC |
| Non-Ferrous Metals Industries | NFM |
| Production of Cement, Lime and Magnesium Oxide | CLM |
| Production of Chlor-Alkali | CAK |
| Production of Polymers | POL |
| Production of Pulp, Paper and Board | PP |
| Production of Speciality Inorganic Chemicals | SIC |
| <i>Refining of Mineral Oil and Gas</i> | REF |
| Slaughterhouses and Animals By-products Industries | SA |
| Smitheries and Foundries Industry | SF |
| Surface Treatment of Metals and Plastics | STM |
| Surface Treatment Using Organic Solvents | STS |
| Tanning of Hides and Skins | TAN |
| Textiles Industry | TXT |
| Waste Incineration | WI |
| Waste Treatment | WT |
| Wood and Wood Products Preservation with Chemicals | WPC |
| Wood-based Panels Production | WBP |
| Reference Document | |
| Economics and Cross-media Effects | ECM |
| General Principles of Monitoring | MON |

Electronic versions of draft and finalised documents are publicly available and can be downloaded from <http://eippcb.jrc.ec.europa.eu/reference/>

PREFACE

1. Status of this document

Unless otherwise stated, references to ‘the Directive’ in this document refer to Directive 2010/75/EU of the European Parliament and the Council on industrial emissions (integrated pollution prevention and control) (Recast).

The original best available techniques (BAT) reference document (BREF) for the Refining of Mineral Oil and Gas (REF) was adopted by the European Commission in 2003. This document is the result of a review of that BREF. The review commenced in January 2008.

This BAT reference document for the Refining of Mineral Oil and Gas forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission, to draw up, review, and where necessary, update BAT reference documents as required by Article 13(1) of the Directive. This document is published by the European Commission pursuant to Article 13(6) of the Directive.

As set out in Article 13(5) of the Directive, the Commission Implementing Decision 2014/738/EU on the BAT conclusions contained in Chapter 5 was adopted on 9 October 2014 and published on 28 October 2014¹.

2. Participants in the information exchange

As required in Article 13(3) of the Directive, the Commission has established a forum to promote the exchange of information, which is composed of representatives from Member States, the industries concerned and non-governmental organisations promoting environmental protection (Commission Decision of 16 May 2011 establishing a forum for the exchange of information pursuant to Article 13 of the Directive 2010/75/EU on industrial emissions (2011/C 146/03), OJ C 146, 17.05.2011, p.3).

Forum members have nominated technical experts constituting the technical working group (TWG) that was the main source of information for drafting this document. The work of the TWG was led by the European IPPC Bureau (of the Commission’s Joint Research Centre).

3. Structure and contents of this document

Chapters 1 and 2 provide general information on the **Refining of Mineral Oil and Gas** and on the industrial processes and techniques used within this sector.

Chapter 3 provides data and information concerning the environmental performance of installations within the sector, and in operation at the time of writing, in terms of current emissions, consumption and nature of raw materials, water consumption, use of energy and the generation of waste.

Chapter 4 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of installations in this sector that were considered in determining the BAT. This information includes, where relevant, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques.

¹ OJ L 307, 28.10.2014, p. 38.

Chapter 5 presents the BAT conclusions as defined in Article 3(12) of the Directive.

Chapter 6 presents information on ‘emerging techniques’ as defined in Article 3(14) of the Directive.

Concluding remarks and recommendations for future work are presented in Chapter 7.

4. Information sources and the derivation of BAT

This document is based on information collected from a number of sources, in particular through the TWG that was established specifically for the exchange of information under Article 13 of the Directive. The information has been collated and assessed by the European IPPC Bureau (of the Commission's Joint Research Centre) who led the work on determining BAT, guided by the principles of technical expertise, transparency and neutrality. The work of the TWG and all other contributors is gratefully acknowledged.

The BAT conclusions have been established through an iterative process involving the following steps:

- identification of the key environmental issues for the sector;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these environmental performance levels were achieved, such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT), their associated emission levels (and other environmental performance levels) and the associated monitoring for this sector according to Article 3(10) of, and Annex III to, the Directive.

Expert judgement by the European IPPC Bureau and the TWG has played a key role in each of these steps and in the way in which the information is presented here.

Where available, economic data have been given together with the descriptions of the techniques presented in Chapter 4. These data give a rough indication of the magnitude of the costs and benefits. However, the actual costs and benefits of applying a technique may depend strongly on the specific situation of the installation concerned, which cannot be evaluated fully in this document. In the absence of data concerning costs, conclusions on the economic viability of techniques are drawn from observations on existing installations.

5. Review of BAT reference documents (BREFs)

BAT is a dynamic concept and so the review of BREFs is a continuing process. For example, new measures and techniques may emerge, science and technologies are continuously developing and new or emerging processes are being successfully introduced into the industries. In order to reflect such changes and their consequences for BAT, this document will be periodically reviewed and, if necessary, updated accordingly.

6. Contact information

All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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SCOPE

This BREF covers certain industrial activities specified in Section 1.2 of Annex I to Directive 2010/75/EU, namely:

- 1.2. Refining of mineral oil and gas.

In particular, this document covers the following processes and activities:

| Activity | Subactivities or processes included in activity |
|--|--|
| Alkylation | All alkylation processes: hydrofluoric acid (HF) sulphuric acid (H ₂ SO ₄) and solid-acid |
| Base oil production | Deasphalting, aromatic extraction, wax processing, and lubricant oil hydrofinishing |
| Bitumen production | All techniques from storage to final product additives |
| Catalytic cracking | All types of catalytic cracking units such as fluid catalytic cracking |
| Catalytic reforming | Continuous, cyclic and semi-regenerative catalytic reforming |
| Coking | Delayed and fluid coking processes. Coke calcination |
| Cooling | Cooling techniques applied in refineries |
| Desalting | Desalting of crude oil |
| Combustion units for energy production | Combustion units burning refinery fuels, excluding units using only conventional or commercial fuels |
| Etherification | Production of chemicals (e.g. alcohols and ethers such as MTBE, ETBE and TAME) used as motor fuels additives |
| Gas separation | Separation of light fractions of the crude oil e.g. refinery fuel gas (RFG), liquefied petroleum gas (LPG) |
| Hydrogen consuming processes | Hydrocracking, hydrotreating, hydrorefining, hydroconversion, hydroprocessing and hydrogenation processes |
| Hydrogen production | Partial oxidation, steam reforming, gas heated reforming and hydrogen purification |
| Isomerisation | Isomerisation of hydrocarbon compounds C ₄ , C ₅ and C ₆ |
| Natural gas plants | Natural gas (NG) processing including liquefaction of NG |
| Polymerisation | Polymerisation, dimerisation and condensation |
| Primary distillation | Atmospheric and vacuum distillation |
| Product treatments | Sweetening and final product treatments |
| Storage and handling of refinery materials | Storage, blending, loading and unloading of refinery materials |
| Visbreaking and other thermal conversions | Thermal treatments such as visbreaking or thermal gas oil process |
| Waste gas treatment | Techniques to reduce or abate emissions to air |
| Waste water treatment | Techniques to treat waste water prior to release |
| Waste management | Techniques to prevent or reduce the generation of waste |

This document does not address the following activities or processes:

- the exploration and production of crude oil and natural gas;
- the transportation of crude oil and natural gas;
- the marketing and distribution of products.

As far as biofuels are concerned, this document covers their handling and processes in conventional refining units within the mineral oil refinery site but it does not cover specific biological or biochemical processes used for their production.

Scope

Finally, the TWG has considered that soil remediation techniques are not included within this document. The reason given is that these techniques are not techniques to prevent or to control emissions. They are techniques used to clean up the soil when it has already been contaminated.

This document is designed to be as comprehensive as possible, taking into consideration the need to avoid duplication with other BREFs. It contains priority information specific to the refinery sector. This means, in particular, that:

- generally applicable information on storage, cooling systems, energy efficiency, monitoring, waste water and waste gas treatments, or economics and cross-media effects pertain to other relevant horizontal BREFs and may have not been developed or even covered in this document;
- generally applicable and specific information on particular processes or units covered by other vertical BREFs **have not been covered**, or may have been only partially covered in this document, for example:
 - the steam cracker for the production of lower olefins, the production of aromatics (i.e. BTX), cyclohexane and cumene, or the alkylation of aromatics, which are covered in the Large Volume Organic Chemicals (LVOC) BREF [85, COM 2003];
 - the production of hydrogen by steam methane reforming, which is covered by the Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers (LVIC-AAF) BREF [92, COM 2007]. This document has been selected to include the generic information on this subject (IEF Strategy to review the Chemical BREFs, March 2007 [250, COM 2007]).
 - the energy production techniques (i.e. boilers and furnaces) when burning exclusively commercial fuels, which are already covered in the Large Combustion Plant (LCP) BREF [7, COM 2006].

Other reference documents which are relevant for the sector covered in this document are the following:

| Reference document | Subject |
|---|--|
| Common Waste Water and Waste Gas Treatment/Management System in the Chemical Sector (CWW) | Waste water management and treatment techniques |
| Industrial Cooling Systems (ICS) | Cooling processes |
| Economics and Cross-media Effects (ECM) | Economics and cross-media effects of techniques |
| Emissions from Storage (EFS) | Storage, blending, loading and unloading of refinery materials |
| Energy Efficiency (ENE) | Energy efficiency and integrated refinery management |
| Large Combustion Plants (LCP) | Combustion of conventional and commercial fuels |
| Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (LVIC-AAF) | Steam reforming and hydrogen purification |
| Large Volume Organic Chemical Industry (LVOC) | Etherification process (MTBE, ETBE and TAME production) |
| Waste Incineration (WI) | Waste incineration |
| Waste Treatment (WT) | Waste treatment |
| General Principles of Monitoring (MON) | Monitoring of emissions to air and water |

The scope of this document does not include matters that only concern safety in the workplace or the safety of products because these matters are not covered by the Directive. They are discussed only where they affect matters within the scope of the Directive.

1 GENERAL INFORMATION

1.1 The purpose of refineries

The purpose of refining is to convert natural raw materials such as crude oil and natural gas into useful saleable products. Crude oil and natural gas are naturally occurring hydrocarbons found in many areas of the world, in varying quantities and compositions. In refineries, these are transformed into different products such as:

- fuels for cars, trucks, aeroplanes, ships and other forms of transport;
- combustion fuels for the generation of heat and power for industry and commercial and domestic use;
- raw materials for the petrochemical and chemical industries;
- speciality products such as lubricating oils, paraffins/waxes and bitumen;
- energy as a by-product in the form of heat (steam) and power (electricity).

In order to manufacture these products, these raw materials are handled and processed in a number of different refining facilities, alone or as a mixture with biofuels. The combination of these processing units which convert crude oil and natural gas into products, including supporting units and facilities, is called a refinery. The market demand for the type of products, the available crude quality and certain requirements set by authorities influence the size, configuration and complexity of a refinery. As these factors vary from location to location, no two refineries are identical.

1.2 Refinery sector in the EU

1.2.1 General

The economic and political worldwide refining industry has undergone considerable changes over time. In recent years, the increased effort in oil and gas exploration and production, as well as cost reductions achieved in these activities, has resulted in the stability of the recognised reserves worldwide.

In 2006, oil and gas provided respectively 42 % and 23 % of the EU-27 final energy consumption. They represent the first and the second most important sources of energy in Europe. About 94 % of the fuels required for transport originated from oil products, while natural gas represented 36 % of energy consumption for services and domestic use, and 20 % of the energy used for power generation.

Despite the progressive increase of biofuels in the transport sector (increasing from less than 0.2 % prior to 2000 to 1.78 % in 2006 for the EU-27), the health and viability of the refining industry remains of critical strategic importance to the EU for maintaining a successful and internationally competitive position for industry as a whole, and for providing competitively priced products to consumers [8, EUROSTAT 2008].

1.2.1.1 Oil refining

In 2012, there were 655 refineries worldwide, with a total capacity of around 4 400 million t/yr. The world's largest refining region is Asia (25 %), followed by North America and Europe (around 20 % each). The top refining countries in the world are the US, followed by China, Russia and Japan. [132, O&Gas Journal 2011]

The refining industry has suffered from a structural overcapacity for distillation for most of the time since the oil crisis in 1973/1974. Only in the early 1980s, early 1990s and late 1990s were attractive margins achieved due to high oil prices at these times. Moreover, severe competition, environmental compliance of the refining industry and regulatory uncertainty have added to the decrease in profitability in certain periods. This long-lasting recession has led oil and gas companies to make significant adjustments in upstream and downstream operations, such as cuts in production costs, innovations in technology, and organisational restructuring. Some big investments have been made to cover diesel demand (e.g. Repsol and Cepsa in Spain - Cartagena, Huelva). But the economic crisis starting in 2008 has led to a decrease in demand on energy products.

Even though some European oil refineries have closed in the last 25 years there has been a progressive increase of crude oil processing capacity since the 1990s, mainly by 'capacity creep' (debottlenecking, improvements in equipment reliability and longer cycles between turnarounds) to cope with a 1 – 2 % increase in product demand per year in Europe. Since 2005, there has been a stabilisation and even a slight decrease of the overall European demand. At the worldwide level, the 'capacity creep' is estimated to be equivalent to six to ten additional global scale refineries going on-stream every year.

Economic experts foresee low margins for future decades due to a low possibility of capacity rationalisation. As a general trend, investment has shifted towards exploration and drilling.

According to the International Energy Agency, 15 European refineries (in CZ, FR, GE, IT and UK) were shut down within the 2008-2013 period with an associated capacity decline of about 8 %. [279, IEA 2013]

Within the context of a constant demand for transportation products with lower environmental impact, the European Union is promoting biofuels, bioproducts and biorefinery investment to reduce EU dependency on fossil-fuel feedstocks and foreign raw materials.

1.2.1.2 Natural gas refining

In parallel to the consumption of petroleum products, the gross inland consumption of natural gas in the EU-27 has progressively increased during the last decades, reaching a peak of around 446 Mtoe in 2005. Despite a slight decrease in 2006 and 2007, EU demand is still expected to grow rather significantly, with a CAGR of around +1.8 % until at least 2020, mainly driven by thermoelectric requirements.

On the other hand, EU indigenous gas production has been stable over the last decade, but is now showing a clear decreasing trend starting in 2004. This production is expected to fall, notably in the UK, Netherlands, Germany and Italy. Consequently, EU-27 dependence on gas importation could rise from a current level of 58 % in 2005 to approximately 81 % in 2025.

This context drives a significant number of projects for new infrastructure imports, both for gaseous feedstock (new pipelines or pipeline connections to the existing network from Russia, the Caspian region, North Africa and the Middle East production fields) and for a number of new LNG terminals. According to some authors, 16 regasification plants devoted to imported liquefied natural gas (LNG) reception, storage and final process were in operation in 2008 in the EU, and five more were under construction. Up to 35 new terminals are under consideration [10, Ruggeri 2008], [11, Van Putten 2008], [12, Basolas 2008].

1.2.2 Feedstock

1.2.2.1 Crude oil feedstock

After a period of steady production in Europe during the 1990s, a decreasing trend has been observed since 2002 and a shift towards lighter (North Sea) crudes, especially in Northern Europe. The world reserve of crude oil seems to guarantee the availability of raw materials for a reasonably long period (~40 years). Table 1.1 shows a summary of the world reserves and the consumption of crude oil per geographical area during the last decade.

Table 1.1: Crude oil reserves and consumption per geographical region (1999 – 2012)

| Proved reserves of oil (thousand million barrels) | 1999 | 2008 | 2009 | 2010 | 2011 | 2012 | 2012 share of total |
|--|---------------|---------------|---------------|---------------|---------------|---------------|------------------------|
| North America | 233 | 216 | 219 | 222 | 221 | 220 | 13.2 % |
| South and Central America | 98 | 199 | 237 | 324 | 327 | 328 | 19.7 % |
| Europe and Eurasia | 97 | 137 | 138 | 138 | 140 | 141 | 8.5 % |
| Middle East | 686 | 754 | 753 | 766 | 798 | 808 | 48.4 % |
| Africa | 85 | 120 | 123 | 125 | 127 | 130 | 7.8 % |
| Asia Pacific | 40 | 42 | 41 | 42 | 41 | 41 | 2.5 % |
| Total world reserves | 1 239 | 1 468 | 1 511 | 1 617 | 1 654 | 1 668 | 100 % |
| Consumption (thousands of barrels daily) | | | | | | | |
| North America | 23 467 | 23 860 | 22 959 | 23 464 | 23 397 | 23 040 | 25.8 % |
| South and Central America | 5 023 | 5 892 | 5 921 | 6 222 | 6 405 | 6 533 | 7.3 % |
| Europe and Eurasia | 19 589 | 20 017 | 19 149 | 19 057 | 18 974 | 18 543 | 20.7 % |
| Middle East | 4 928 | 7 185 | 7 526 | 7 861 | 7 992 | 8 354 | 9.3 % |
| Africa | 2 467 | 3 218 | 3 302 | 3 463 | 3 359 | 3 253 | 3.6 % |
| Asia Pacific | 20 606 | 25 881 | 26 205 | 27 766 | 28 754 | 29 781 | 33.3 % |
| Total world consumption | 76 080 | 86 053 | 84 062 | 87 833 | 88 881 | 89 504 | 100 % |
| <u>Proved reserves of oil:</u> quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions. | | | | | | | |
| <u>Consumption:</u> inland demand plus international aviation and marine bunkers and refinery fuel and loss. Consumption of fuel ethanol and biodiesel is also included. | | | | | | | |
| <i>Source:</i> [277, BP 2013] | | | | | | | |

The advent of North Sea crude oils and the continuous increase in the production of these light, low-sulphur crudes is mainly responsible for the lowering of the average sulphur content of the crude oils processed in European refineries. Since 1985, the average sulphur content has fluctuated at around 1.0 % to 1.1 %. However, the difference between type of crude processed in each European region should be noted, i.e. an average of 1.17 % S in the crude oils processed in the refineries of North West Europe, an average of 0.91 % S in the Atlantic region, 1.2 % S in the Mediterranean and 0.64 % S in the 'Others'. The availability of the type of crude oil going to refineries is not the same.

Some local factors for these differences are the following:

- location close to oilfields where low-sulphur crudes are produced (freight for crude from the North Sea to the Mediterranean costs up to USD 1/bbl, so low-sulphur crudes from the North Sea are rarely processed in the Mediterranean area);
- refinery equipped with insufficient desulphurisation/upgrading capacity to process (heavy) high-sulphur crudes;
- exclusion from markets where high-sulphur products can be sold (e.g. bitumen, bunker fuel);
- some other form of specialisation in the use of low-sulphur crudes (e.g. base oil production).

Figure 1.1 shows the sulphur balance trend up to 2010 for EU refineries.

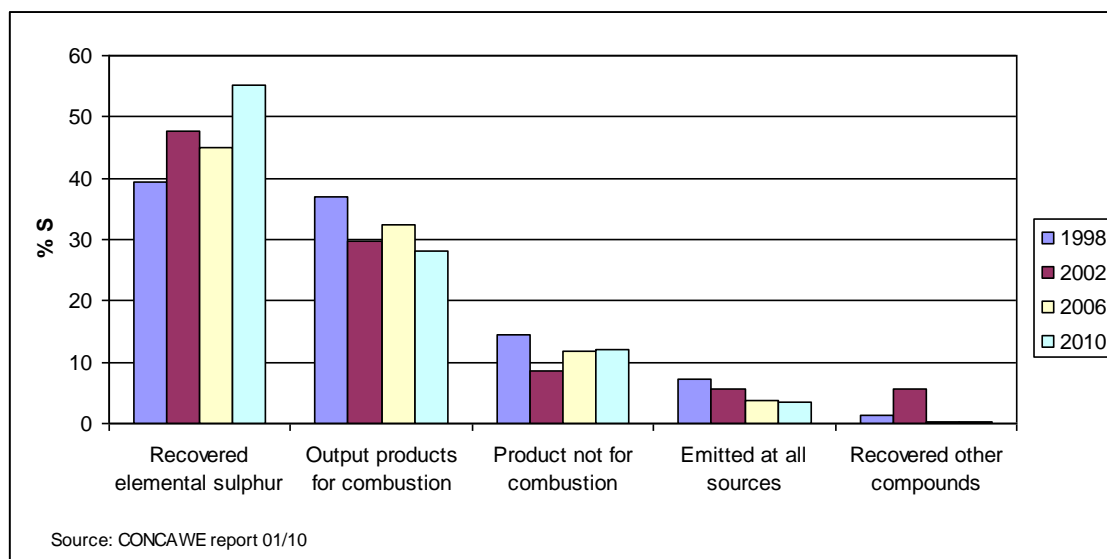


Figure 1.1: Refinery sulphur balance trend up to 2010

1.2.2.2 Biofuels feedstock growth

Specific support policies worldwide aim to replace fossil fuel consumption with biofuels and stimulate biofuel production and expansion in domestic markets. They result in a fast-growing production of these products (mainly bioethanol and biodiesel), which are then blended with petroleum products for use as transport fuels.

Figure 1.2 shows the quota (%) on blending versus the target set by the EU Directive on biofuels (2003/30/EC). Obviously, this has led to an increase of the European consumption of these products for transport that are normally commercialised by the large oil companies.

Table 1.2 shows the consumption of biodiesel and ethanol for transport in the EU in the year 2009 in tonnes of oil equivalent (toe).

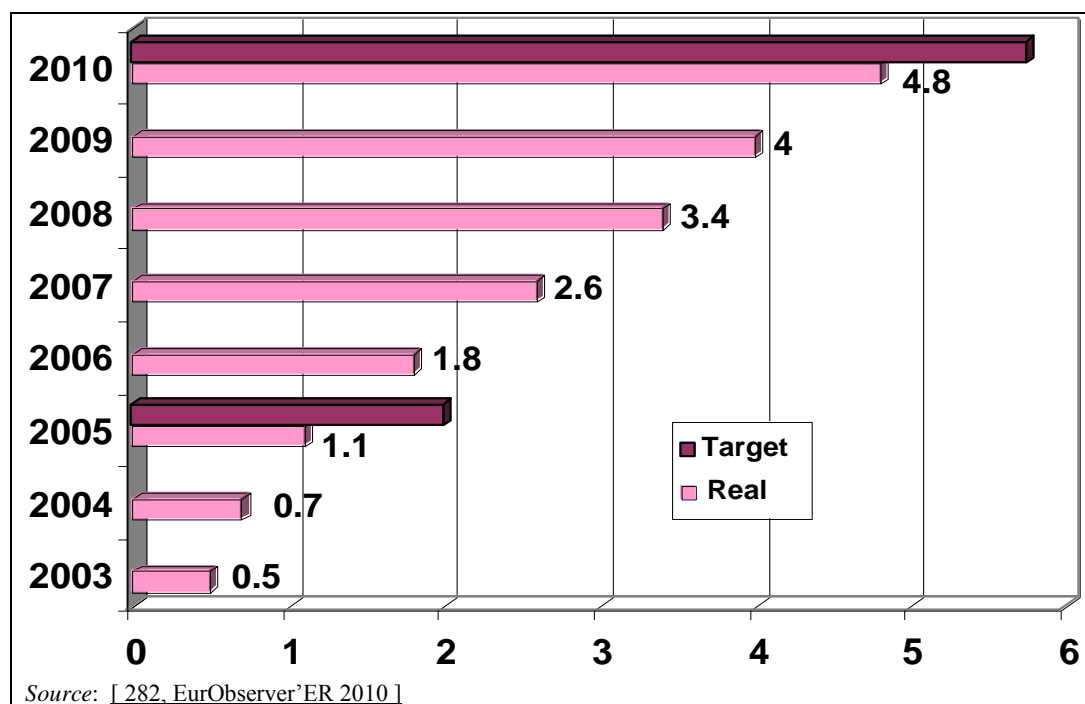


Figure 1.2: Percentage of biofuel blend

Table 1.2: Biofuels consumption for transport by country (2009 - tonnes of oil equivalent)

| Country | Bioethanol | Biodiesel | Other | TOTAL |
|---|------------------|------------------|----------------|-------------------|
| Germany | 581 686 | 2 224 349 | 88 272 | 2 894 307 |
| France | 455 933 | 2 055 556 | | 2 511 489 |
| Italy | 118 014 | 1 048 988 | | 1 167 002 |
| Spain | 152 193 | 894 335 | | 1 046 528 |
| UK | 159 000 | 822 872 | | 981 872 |
| Poland | 136 043 | 568 997 | | 705 040 |
| Austria | 64 249 | 424 901 | 13 369 | 502 519 |
| Sweden | 199 440 | 159 776 | 35 015 | 394 231 |
| Netherlands | 138 650 | 228 886 | | 367 536 |
| Belgium | 37 577 | 221 252 | | 258 829 |
| Portugal | 0 | 231 468 | | 231 468 |
| Romania | 53 274 | 131 328 | | 184 602 |
| Hungary | 64 488 | 119 303 | | 183 791 |
| Czech Rep. | 51 097 | 119 809 | | 170 906 |
| Finland | 79 321 | 66 280 | | 145 601 |
| Ireland | 19 733 | 54 261 | | 73 994 |
| Slovakia | 6 820 | 55 041 | | 61 861 |
| Greece | 0 | 57 442 | | 57 442 |
| Lithuania | 14 091 | 37 770 | | 51 861 |
| Luxembourg | 740 | 39 915 | 498 | 41 153 |
| Slovenia | 1 859 | 27 993 | | 29 852 |
| Cyprus | 0 | 15 024 | | 15 024 |
| Bulgaria | 0 | 6 186 | | 6 186 |
| Latvia | 1 120 | 3 570 | | 4 690 |
| Denmark | 3 913 | 243 | | 4 156 |
| Malta | 0 | 583 | | 583 |
| Estonia | NA | NA | NA | |
| TOTAL EU-27 | 2 339 241 | 9 616 128 | 137 154 | 12 092 523 |
| <i>Source: [282, EurObserver'ER 2010]</i> | | | | |

Bioethanol

Worldwide, the US and Brazil dominate bioethanol production, as seen in Figure 1.3. Worldwide production amounted to 22 Mtoe in 2006, with almost half of it produced in the US from corn crops grown in the Midwest, representing 2 – 3 % of the country's fuel.

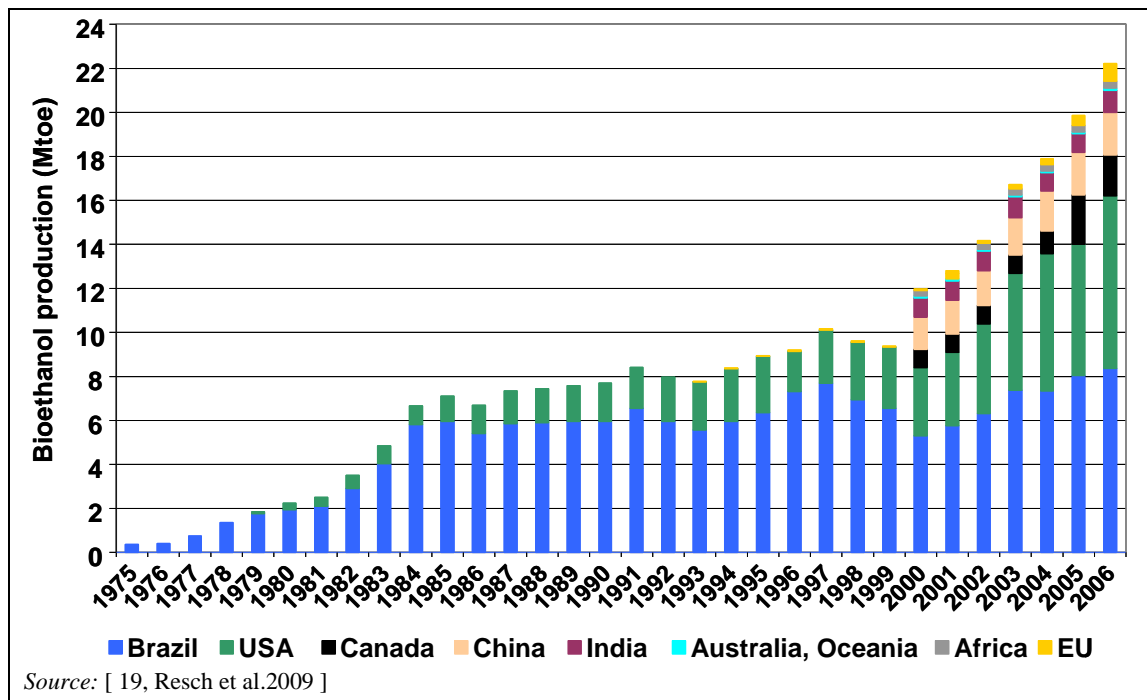


Figure 1.3: World bioethanol fuel production

Biodiesel

Biodiesel remains a small fraction of the fuel used worldwide but, as seen in Figure 1.4, has experienced strong growth rates in the last years, especially in Europe where biodiesel (mainly from rapeseed and sunflower oil) accounts for 75 % of the total EU biofuel production. In 2006, the European Union produced 4.7 Mt (3.2 Mtoe), experiencing a 66 % growth compared to 2005. In 2007, this capacity grew more than double to 11 Mt (7.5 Mtoe) in Europe. Germany is the world's leading biodiesel producer, making 40 % of the world total in recent years, followed by France and Italy.

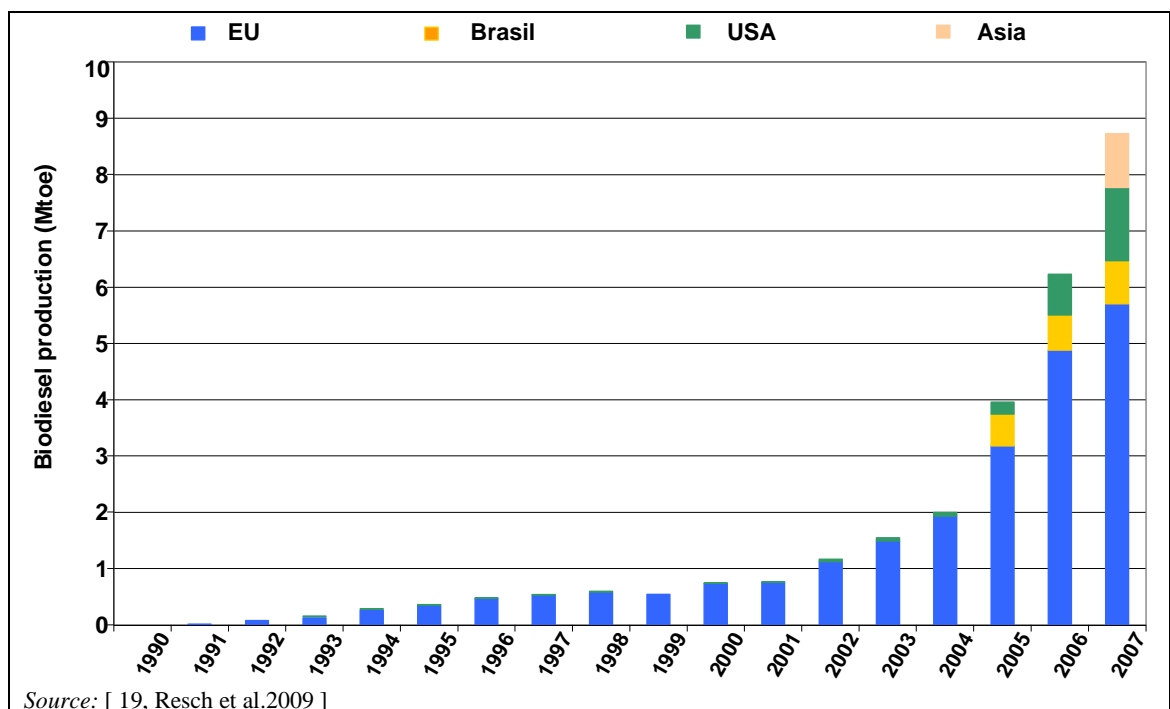


Figure 1.4: World biodiesel fuel production (European Biodiesel Board, EU Barometer, Biofuels Global Potentials 2007)

According to the European Biodiesel Board, Europe is the largest biodiesel market in the world at the time of writing. In 2007, Europe consumed over 7.5 Mm³ (5.15 Mtoe) of biodiesel. In December 2007, biodiesel imports to Europe had reached 0.8 Mt (0.6 Mtoe), which corresponds to a 500 % increase from 2006. Over 50 % of feedstock imports to Europe in 2007 came from Russia and Ukraine, accounting for 0.4 Mt (0.27 Mtoe).

1.2.2.3 Natural gas feedstock

In 2005, proven world gas reserves were equal to 60 years of gas production at current rates. Since 2005, the proven reserves increased faster than gas consumption and estimated reserves could represent the equivalent of another 200 years of consumption.

The highest percentage of gas supplied in the EU-27 comes from indigenous production, covering 37 % of total net supplies (432 Mtoe) in 2007. The main external sources are Russia (24 %), Norway (19 %), and Algeria (10 %). The decrease in the EU-27 indigenous production over the period is mainly compensated for by the growing imports from Norway.

Table 1.3 shows the proven reserves of natural gas (see table for definitions) [277, BP 2013].

Table 1.3: Proven reserves of natural gas (2012)

| | At end 1989 | At end 1999 | At end 2009 | At end 2012 | 2012 Share of total | Reserves- to- production R/P Ratio (years) |
|-----------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------------------|--|
| | Trillion cubic metres | Trillion cubic metres | Trillion cubic metres | Trillion cubic metres | | |
| Total North America | 9.5 | 7.3 | 9.8 | 10.8 | 5.9 % | 12.1 |
| of which USA | 4.7 | 4.7 | 7.7 | 8.8 | 4.8 % | 12.5 |
| Canada | 2.7 | 1.7 | 1.7 | 2 | 1.1 % | 12.7 |
| Total S. and Cent. America | 4.8 | 6.8 | 7.0 | 7.5 | 4.1 % | 42.8 |
| Total Europe and Eurasia | 37 | 41.6 | 47.3 | 58.4 | 31.7 % | 56.4 |
| of which Azerbaijan | NA | 0.9 | 0.9 | 0.9 | 0.5 % | 57.1 |
| Denmark | 0.1 | 0.1 | 0.1 | - | - | - |
| Germany | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 % | 6.1 |
| Italy | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 % | 7 |
| Kazakhstan | NA | 1.2 | 1.3 | 1.3 | 0.7 % | 65.6 |
| The Netherlands | 1.6 | 1.6 | 1.2 | 1.0 | 0.5 % | 16.3 |
| Norway | 1.7 | 1.2 | 2.0 | 2.1 | 1.1 % | 18.2 |
| Poland | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 % | 28.3 |
| Romania | 0.1 | 0.3 | 0.6 | 0.1 | 0.1 % | 9.3 |
| Russian Federation | NA | 29.8 | 31.1 | 32.9 | 17.9 % | 55.6 |
| Turkmenistan | NA | 2.3 | 7.3 | 17.5 | 9.5 % | (*) |
| Ukraine | NA | 0.7 | 0.7 | 0.6 | 0.3 % | 34.6 |
| United Kingdom | 0.6 | 1.3 | 0.3 | 0.2 | 0.1 % | 6 |
| Uzbekistan | NA | 1.1 | 1.1 | 1.1 | 0.6 % | 19.7 |
| Other Europe and Eurasia | 32.1 | 0.5 | 0.4 | 0.3 | 0.2 % | 29.2 |
| Total Middle East | 37.8 | 54.7 | 75.9 | 80.5 | 43.7 % | (*) |
| Total Africa | 8.5 | 11.4 | 14.8 | 11.5 | 6.2 % | 67.1 |
| Total Asia Pacific | 9.5 | 12.1 | 15.2 | 15.5 | 8.4 % | 31.5 |
| Total World | 107.1 | 134 | 170 | 184.2 | 100 % | 55.7 |

Proven reserves: quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions.

Reserves-to-production (R/P) ratio: reserves remaining at the end of any year divided by the production in that year. The result is the length of time that these remaining reserves would last while having the same production rate.

(*) >100 years

Source: [277, BP 2013]

1.2.3 European refining capacity

1.2.3.1 European oil refining capacity

European refineries are characterised by an excess in primary processing capacity, and by some 'misfits' (incompatibility between production and market demand) and excess in conversion capacity. European downstream sectors have too many refineries producing too much gasoline.

Table 1.6 shows, per type of process, the charge and production capacity of European oil refineries for the European Union (EU-27) and for EU+ Countries, which will correspond hereafter in this document to the EU-27 enlarged by associated and official candidate Countries: Croatia, Former Yugoslav Republic of Macedonia (FYROM), Norway, Switzerland and Turkey. The crude oil capacity of the 106 plants operating in the EU-27 at the beginning of 2013 was below 1 billion tonnes per year. This corresponded to 17 % of the entire global capacity, whereas the US capacity accounted for 20 % of the entire global capacity. The average individual capacity of European sites was about 7.9 Mm³/yr, similar to the other parts of the

world. As a comparison, at the same time, the refining crude oil capacity of the 125 plants operated in the US was reaching around 1 billion m³/yr, leading to an individual average capacity of 8.2 Mm³/yr. At the global level, 655 plants were in operation at the beginning of 2012, with an average individual capacity of 7.8 Mm³/yr for an overall crude capacity of around 5 billion m³/yr in 2012 [132, O&Gas Journal 2011].

Refining distillation capacity decreased substantially in the early 1980s following the oil price shocks of the 1970s. At the same time, the industry had to invest heavily in conversion capacity to convert fuel oil and adapt to demand for lighter transport fuels. Official figures for nameplate capacity show small further capacity reductions until the end of 1995. Combined with a slow rise in demand since 1986 this has increased apparent distillation capacity utilisation from a low point of 60 % in 1981 to an average above 90 % in 1997, higher in northern Europe and lower in southern Europe.

There are differences in supply and demand balances between different countries, with Germany and Spain in particular having a large supply deficit. The growth of oil products demand in Iberia has been well above the average for the EU, particularly in transport fuels. However, oil demand growth in the 1990s showed the Mediterranean region to be in line with the rest of Europe.

For the future, according to the Commission [72, COM 2010] and based on specific modelling, the investments required to upgrade EU+3 (including Switzerland, Norway and Turkey) refining capacities could reach EUR 17.8 billion (including 3.3 for international maritime organisation (IMO) changes) between 2005 and 2030. These amounts would be mainly dedicated to extra gas oil hydrodesulphurisation units. The CONCAWE projections, keeping trade levels constant for the period 2005 – 2030, indicate it would require EUR 29.2 billion of investment.

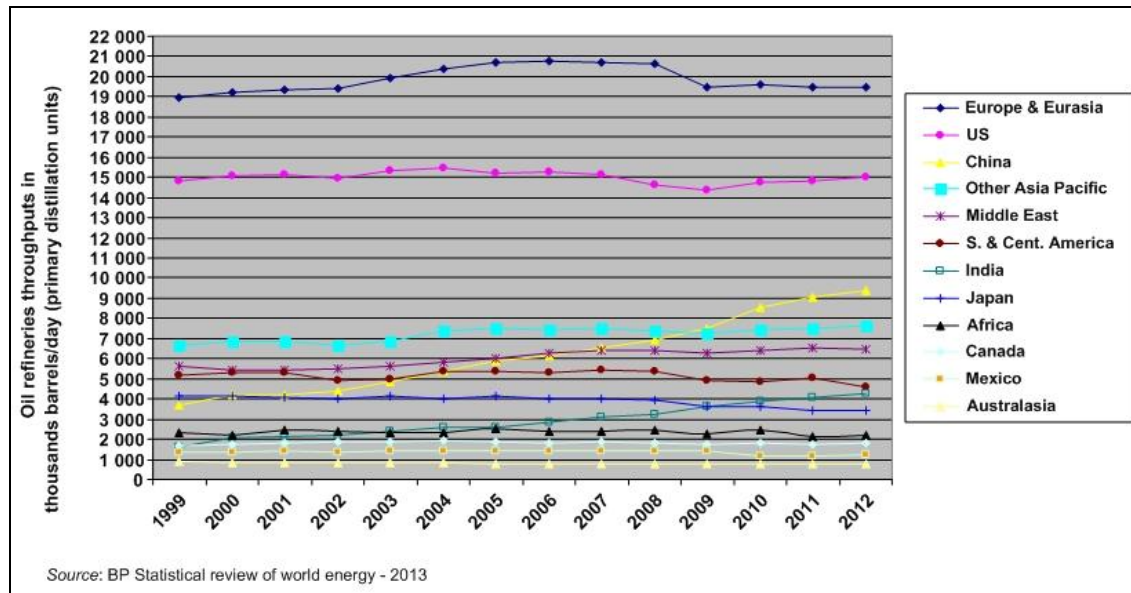


Figure 1.5: Global oil refining throughputs

1.2.3.2 European natural gas refining capacity

There has been a mild decline in the European gas refining output. The following tables give some background information on the worldwide production and consumption of gas within the period 1999 – 2012. Member States from the EU-27 are shown in italics.

Table 1.4: Worldwide gas production (1999 – 2012)

| | Production expressed as billions of cubic metres | | | | | 2012 share of total |
|-----------------------------------|---|--------------|---------------|---------------|---------------|---------------------------|
| | 1999 | 2009 | 2010 | 2011 | 2012 | |
| Total North America | 748 | 807.4 | 821.1 | 866.5 | 896.4 | 26.8 % |
| of which US | 533 | 584.0 | 603.6 | 648.5 | 681.4 | 20.4 % |
| Canada | 177 | 164.0 | 159.9 | 159.7 | 156.5 | 4.6 % |
| Total S. and Cent. America | 92 | 155.9 | 166.6 | 171.5 | 177.3 | 5.3 % |
| Total Europe and Eurasia | 913.4 | 958.8 | 1031.2 | 1039.9 | 1035.4 | 30.7 % |
| of which Azerbaijan | 5.4 | 14.8 | 15.1 | 14.8 | 15.6 | 0.5 % |
| Denmark | 7.8 | 8.4 | 8.2 | 7.1 | 6.4 | 0.2 % |
| Germany | 17.8 | 12.2 | 10.6 | 10.0 | 9.0 | 0.3 % |
| Italy | 16.0 | 7.3 | 7.6 | 7.7 | 7.8 | 0.2 % |
| Kazakhstan | 6.6 | 17.8 | 17.6 | 19.3 | 19.7 | 0.6 % |
| Netherlands | 60.2 | 62.7 | 70.5 | 64.2 | 63.9 | 1.9 % |
| Norway | 48.5 | 104.8 | 107.7 | 101.7 | 114.9 | 3.4 % |
| Poland | 3.4 | 4.1 | 4.1 | 4.3 | 4.2 | 0.1 % |
| Romania | 14.0 | 11.3 | 10.9 | 10.9 | 10.9 | 0.3 % |
| Russian Federation | 535.7 | 527.7 | 588.9 | 607.0 | 592.3 | 17.6 % |
| Turkmenistan | 20.6 | 36.4 | 42.4 | 59.5 | 64.4 | 1.9 % |
| Ukraine | 16.4 | 19.2 | 18.1 | 18.6 | 18.6 | 0.6 % |
| United Kingdom | 99.1 | 62.4 | 59.7 | 47.6 | 41.0 | 1.2 % |
| Uzbekistan | 50.3 | 60.0 | 59.6 | 57.0 | 56.9 | 1.7 % |
| Other Europe and Eurasia | 11.4 | 9.7 | 10.2 | 10.2 | 9.8 | 0.3 % |
| Total Middle East | 195 | 407.3 | 472.7 | 518.7 | 548.4 | 16.3 % |
| Total Africa | 119 | 200.4 | 214.3 | 211.2 | 216.2 | 6.4 % |
| Total Asia Pacific | 263 | 439.6 | 486.5 | 483.6 | 490.2 | 14.5 % |
| Total world | 2 330 | 2 970 | 3 192 | 3 291 | 3 364 | 100.0 % |

Source: [277, BP 2013]

Table 1.5: Worldwide gas consumption (1999 – 2012)

| | Consumption expressed as billions of cubic metres | | | | | 2012 share of total |
|---|--|--------------|--------------|--------------|--------------|---------------------------|
| | 1999 | 2009 | 2010 | 2011 | 2012 | |
| Total North America | 761 | 816 | 850 | 868 | 907 | 27.4 % |
| of which US | 634 | 649 | 682 | 691 | 722 | 21.8 % |
| Canada | 87 | 95 | 95 | 101 | 101 | 3 % |
| Total S. and Cent. America | 90 | 137 | 152 | 156 | 165 | 5 % |
| Total Europe and Eurasia | 967 | 1 050 | 1 130 | 1 106 | 1 083 | 32.6 % |
| of which Austria | 8.5 | 9.3 | 10.1 | 9.5 | 9.0 | 0.3 % |
| Azerbaijan | 5.4 | 7.8 | 7.4 | 8.1 | 8.5 | 0.5 % |
| Belarus | 14.8 | 16.1 | 19.7 | 18.3 | 18.6 | 0.6 % |
| Belgium | 14.8 | 16.8 | 18.8 | 16.6 | 16.9 | 0.5 % |
| Bulgaria | 3.0 | 2.3 | 2.6 | 2.9 | 2.7 | 0.1 % |
| Czech Republic | 8.6 | 8.2 | 9.3 | 8.4 | 8.2 | 0.2 % |
| Denmark | 5.0 | 4.4 | 5.0 | 4.2 | 3.9 | 0.1 % |
| Finland | 3.7 | 3.6 | 3.9 | 3.4 | 3.1 | 0.1 % |
| France | 37.7 | 42.6 | 47.4 | 40.9 | 42.5 | 1.3 % |
| Germany | 80.2 | 78.0 | 83.3 | 74.5 | 75.2 | 2.3 % |
| Greece | 1.5 | 3.4 | 3.7 | 4.5 | 4.2 | 0.1 % |
| Hungary | 11.0 | 10.2 | 10.9 | 10.4 | 9.7 | 0.3 % |
| Ireland | 3.3 | 4.8 | 5.2 | 4.6 | 4.5 | 0.1 % |
| Italy | 62.2 | 71.5 | 76.1 | 71.3 | 68.7 | 2.1 % |
| Kazakhstan | 6.2 | 7.8 | 8.2 | 9.2 | 9.5 | 0.3 % |
| Lithuania | 2.4 | 2.7 | 3.1 | 3.4 | 3.3 | 0.1 % |
| Netherlands | 38.5 | 38.9 | 43.6 | 38.1 | 36.4 | 1.1 % |
| Norway | 3.6 | 4.1 | 4.1 | 4.3 | 4.3 | 0.1 % |
| Poland | 10.3 | 14.4 | 15.5 | 15.7 | 16.6 | 0.5 % |
| Portugal | 2.3 | 4.7 | 5.1 | 5.2 | 4.7 | 0.1 % |
| Romania | 17.2 | 13.3 | 13.6 | 13.9 | 13.5 | 0.4 % |
| Russian Federation | 352.8 | 389.6 | 414.1 | 424.6 | 416.2 | 12.5 % |
| Slovakia | 6.4 | 4.9 | 5.6 | 5.2 | 6.0 | 0.2 % |
| Spain | 15.0 | 34.6 | 34.6 | 32.2 | 31.4 | 0.9 % |
| Sweden | 0.8 | 1.1 | 1.6 | 1.3 | 1.1 | 0.05 % |
| Switzerland | 2.7 | 3.0 | 3.3 | 3.0 | 3.2 | 0.1 % |
| Turkey | 12.4 | 35.7 | 39.0 | 45.7 | 46.3 | 1.4 % |
| Turkmenistan | 11.0 | 19.9 | 22.6 | 25.0 | 23.3 | 0.7 % |
| Ukraine | 70.9 | 47.0 | 52.1 | 53.7 | 49.6 | 1.5 % |
| United Kingdom | 93.6 | 91.2 | 99.2 | 82.8 | 78.3 | 2.4 % |
| Uzbekistan | 47.8 | 43.5 | 45.5 | 49.1 | 47.9 | 1.4 % |
| Other Europe and Eurasia | 13.4 | 14.0 | 15.1 | 15.7 | 16.1 | 0.5 % |
| Total Middle East | 181 | 345 | 377 | 395 | 412 | 12.4 % |
| Total Africa | 52 | 100 | 108 | 114 | 123 | 3.7 % |
| Total Asia Pacific | 270 | 497 | 560 | 594 | 625 | 18.8 % |
| Total world | 2 320 | 2 944 | 3 176 | 3 232 | 3 314 | 100.0 % |
| The difference between the world consumption figures and the world production statistics is due to variations in stocks at storage facilities | | | | | | |
| Source: [277, BP 2013] | | | | | | |

Table 1.6: EU+ capacity for mineral oil refining

| Charge capacity in Mm ³ /yr | | | | | | | | | |
|--|----------------------|--------------|---------------------|-------------|--------------------|--------------------|---------------------|-------------------------|-------------------------|
| Country | No of oil refineries | Crude | Vacuum distillation | Coking | Thermal operations | Catalytic cracking | Catalytic reforming | Catalytic hydrocracking | Catalytic hydrotreating |
| Austria | 1 | 12.1 | 3.8 | | 1.0 | 1.5 | 1.9 | | 8.1 |
| Belgium | 4 | 42.9 | 14.5 | | 1.7 | 7.8 | 6.1 | | 39.9 |
| Bulgaria | 1 | 6.7 | 2.9 | | 1.2 | 1.4 | 0.2 | | 3.7 |
| Cyprus | 0 | | | | | | | | |
| Czech Republic | 4 | 10.6 | 4.6 | | 1.0 | | 1.6 | 2.0 | 6.0 |
| Denmark | 2 | 10.1 | 1.3 | | 3.7 | | 1.3 | | 2.5 |
| Estonia | 0 | | | | | | | | |
| Finland | 2 | 15.1 | 8.5 | | 2.0 | 3.3 | 2.9 | 5.2 | 17.3 |
| France | 11 | 86.9 | 35.1 | | 6.8 | 18.1 | 12.7 | 4.2 | 68.4 |
| Germany | 13 | 140.3 | 63.6 | 6.1 | 14.4 | 20.3 | 23.5 | 11.8 | 116.74 |
| Greece | 4 | 24.5 | 8.8 | | 2.8 | 4.4 | 2.9 | 2.5 | 21.0 |
| Hungary | 1 | 9.3 | 4.5 | 1.0 | 0.8 | 1.4 | 1.7 | | 7.0 |
| Ireland | 1 | 4.1 | | | | | 0.6 | | 2.6 |
| Italy | 15 | 135.6 | 47.3 | 2.6 | 26.0 | 18.7 | 16.7 | 17.6 | 72.58 |
| Latvia | 0 | | | | | | | | |
| Lithuania | 1 | 11.0 | 5.2 | | 1.7 | 2.5 | 2.7 | | 8.9 |
| Luxembourg | 0 | | | | | | | | |
| Malta | 0 | | | | | | | | |
| Netherlands | 5 | 68.9 | 40.8 | 2.4 | 5.3 | 5.9 | 8.6 | 11.5 | 59.0 |
| Poland | 5 | 28.6 | 15.4 | | | 1.9 | 3.9 | 8.5 | 15.1 |
| Portugal | 2 | 17.7 | 5.1 | | 2.1 | 2.4 | 2.9 | 0.5 | 11.7 |
| Romania | 9 | 31.2 | 15.9 | 4.0 | 2.2 | 6.4 | 3.6 | 0.1 | 13.8 |
| Slovakia | 1 | 6.7 | 3.2 | | | 1.0 | 1.2 | 2.4 | 5.1 |
| Slovenia | 0 | 0.8 | | | | | | | |
| Spain | 10 | 73.8 | 24.0 | 3.5 | 8.7 | 11.1 | 11.4 | 7.6 | 47.9 |
| Sweden | 5 | 25.4 | 7.9 | | 3.9 | 1.7 | 4.1 | 2.8 | 15.6 |
| United Kingdom | 9 | 102.5 | 50.3 | 3.7 | 6.2 | 25.8 | 19.7 | 2.1 | 73.8 |
| EU-27 | 106 | 864.8 | 362.6 | 23.4 | 91.5 | 135.4 | 130.2 | 78.9 | 616.7 |
| % World capacity | 17 % | 17 % | 21 % | 9 % | 41 % | 16 % | 20 % | 25 % | 23 % |
| Croatia | 2 | 14.5 | 5.1 | 0.3 | 1.4 | 3.0 | 2.9 | 0.7 | 4.0 |
| FYROM | 1 | 2.9 | | | | | 0.6 | | 1.3 |
| Norway | 2 | 18.5 | | 1.4 | 1.9 | 2.8 | 2.0 | | 7.3 |
| Switzerland | 2 | 4.2 | | | | 1.2 | 0.7 | | 1.9 |
| Turkey | 6 | 41.4 | 11.7 | | 1.4 | 1.7 | 3.8 | 3.1 | 15.4 |
| EU+ | 119 | 946.4 | 379.3 | 25.1 | 96.0 | 144.1 | 140.3 | 82.7 | 646.5 |
| % World capacity | 19 % | 19 % | 22 % | 9 % | 44 % | 17 % | 21 % | 26 % | 24 % |

| Production capacity in Mm ³ /yr (except units mentioned specifically) | | | | | | | | | | |
|---|-------------|--------------------------------|-------------|---------------|------------------------|----------------|-----------------------------------|---------------|------------------|-------------|
| Country | Alkylation | Polymerisation dimerisation | Aromatics | Isomerisation | Base oil production | Etherification | Hydrogen (MNm ³ /d) | Coke (t/d) | Sulphur (t/d) | Bitumen |
| Austria | | | | 0.84 | | 0.09 | | | 180 | 0.09 |
| Belgium | 1.02 | | | | | 0.22 | 2.79 | | 971 | 1.54 |
| Bulgaria | 0.15 | | 0.12 | | | 0.05 | 0.29 | | 63 | 0.09 |
| Czech Rep. | | | 0.04 | 0.42 | 0.13 | 0.13 | 3.17 | | 144 | 0.63 |
| Denmark | | | | 0.37 | | | | | | 0.46 |
| Finland | 0.45 | 0.03 | | | 0.31 | 0.33 | 4.53 | | 540 | 0.39 |
| France | 1.55 | 0.17 | 0.17 | 2.81 | 1.72 | 0.27 | 3.45 | | 1362 | 1.47 |
| Germany | 1.79 | 0.48 | 4.17 | 5.47 | 0.83 | 0.76 | 21.86 | 3813 | 2914 | 3.52 |
| Greece | 0.14 | 0.10 | 0.53 | 1.37 | 0.20 | 0.23 | 0.67 | | 519 | 0.98 |
| Hungary | 0.19 | | 0.70 | 0.20 | 0.35 | 0.07 | 2.16 | 600 | 226 | 0.37 |
| Ireland | | | | 0.44 | | | 0.29 | | 4 | |
| Italy | 2.34 | 0.09 | 0.78 | 6.51 | 1.39 | 0.68 | 8.65 | 2046 | 1776 | 0.91 |
| Lithuania | | 0.42 | | 1.10 | | 0.16 | 0.71 | | 320 | |
| Netherlands | 0.9 | | 4.00 | 0.51 | 0.67 | 0.16 | 10.16 | | 1726 | 0.62 |
| Poland | 0.20 | | 0.60 | 1.35 | 1.03 | 0.15 | 4.73 | | 560 | 1.94 |
| Portugal | 0.31 | | 1.00 | | | | 2.42 | | 252 | |
| Romania | 0.13 | | 0.45 | 0.22 | 0.60 | 0.08 | 0.51 | 2555 | 143 | 0.80 |
| Slovakia | 0.26 | | 0.54 | 0.35 | 0.12 | 0.09 | 2.54 | | 270 | 0.15 |
| Slovenia | | | | | | | | | | |
| Spain | 0.98 | | 1.5 | 2.09 | 0.56 | 0.56 | 8.50 | 3565 | 1762 | 1.54 |
| Sweden | | 0.20 | | 1.66 | | | 1.52 | | 334 | 1.59 |
| UK | 5.35 | 0.79 | 0.85 | 6.99 | 1.39 | 0.23 | 3.60 | 2400 | 792 | 1.65 |
| EU-27 | 16 | 2 | 15 | 33 | 9 | 4 | 83 | 14 979 | 14 858 | 19 |
| % World capacity | 13 % | 20 % | 19 % | 34 % | 20 % | 38 % | 21 % | 7 % | 18 % | 18 % |
| Croatia | | | 0.55 | 0.32 | 0.03 | | | 200 | 123 | |
| FYROM | | | | 0.25 | | | | | | |
| Norway | | 0.64 | | 0.22 | | | | 610 | 20 | |
| Switzerland | | 0.22 | | 0.37 | | | 0.79 | | | |
| Turkey | | | | 0.82 | 0.34 | | 6.16 | 180 | 315 | 1.17 |
| EU+ | 16 | 3 | 16 | 35 | 10 | 4 | 89 | 15 969 | 15 316 | 20 |
| % World capacity | 13 % | 28 % | 20 % | 36 % | 21 % | 38 % | 22 % | 8 % | 18 % | 19 % |
| NB for Table 1.6 (first part): | | | | | | | | | | |
| - Vacuum distillation has been included in primary distillation sections in this document. | | | | | | | | | | |
| - Thermal operations include visbreaking (within this document) and thermal cracking (within LVOC BREF). | | | | | | | | | | |
| - Catalytic hydrocracking, hydrotreating and hydrotreatment are included in hydrogen-consuming processes. | | | | | | | | | | |
| NB for Table 1.6 (second part): | | | | | | | | | | |
| - Aromatic production is included in the LVOC BREF, although some refineries have it. | | | | | | | | | | |
| Source: [9, Koottungal 2008], [132, O&Gas Journal 2011], reviewed by TWG, 2013 | | | | | | | | | | |

1.2.4 Product market

1.2.4.1 Petroleum products

The European market is characterised by a growing demand for petrochemicals, kerosene and diesel, and a declining demand for gasoline, light heating oil and heavy fuel oil. There is ongoing competition because of the increasing capacity in the Middle East and Asia.

In the particular case of automotive fuels, and despite the progressive technical adaptation of European sites which lead them to produce (on average) more middle distillates than in every other region in the world except Asia (as seen in Table 1.7), EU refineries are still not producing the mix demanded by EU consumers due to their technical design. They cannot satisfy the existing demand for diesel and they continue to produce gasoline in excess. Due to favourable taxation, the share of the diesel fleet has risen from 23 % in 1996 to 53 % in 2006, and is expected to increase to 60 – 65 % over the next decade.

Table 1.7: Product group consumption per region – Evolution from 2002 to 2012

| Product Consumption (Thousands of barrels per day) | Light distillates | | Middle distillates | | Fuel oil | | Others | |
|---|-------------------|--------------|--------------------|--------------|-------------|-------------|--------------|--------------|
| | 2002 | 2012 | 2002 | 2012 | 2002 | 2012 | 2002 | 2012 |
| North America | 10514 | 10594 | 6654 | 6417 | 1187 | 635 | 5442 | 5394 |
| (of which US) | (9167) | (9221) | (5735) | (5281) | (686) | (343) | (4172) | (3976) |
| South and Central America | 1401 | 1898 | 1706 | 2535 | 752 | 678 | 1146 | 1422 |
| Europe | 4125 | 2976 | 6939 | 7389 | 1866 | 1063 | 3040 | 2724 |
| Former Soviet Union | 1056 | 1352 | 1039 | 1453 | 635 | 418 | 863 | 1169 |
| Middle East | 1175 | 1886 | 1740 | 2753 | 1374 | 1916 | 1163 | 1799 |
| Africa | 602 | 873 | 1135 | 1641 | 388 | 431 | 443 | 577 |
| Asia Pacific | 6198 | 9281 | 8182 | 10487 | 3383 | 3633 | 4323 | 6379 |
| (of which China) | (1359) | (3182) | (1785) | (3741) | (783) | (820) | (1335) | (2477) |
| (of which Japan) | (1728) | (1632) | (1944) | (1360) | (632) | (811) | (1053) | (911) |
| World | 25071 | 28862 | 27395 | 32675 | 9854 | 8773 | 16421 | 19463 |
| Light distillates: aviation, motor gasolines and light distillate feedstock (LDF). Middle distillates: jet and heating kerosines, gas and diesel oils. Fuel oil: marine bunkers and crude oil used directly as fuel. Others: refinery gas, liquefied petroleum gas (LPG), solvents, petroleum coke, lubricants, bitumen, wax, other refined products and refinery fuel and loss. | | | | | | | | |
| Source: [277, BP 2013] | | | | | | | | |

According to the Commission [72, COM 2010], the evolution of the petroleum product demand mix in the EU between 1990 and 2008 is the following:

- the share of jet fuel and kerosene has increased from 5.5 % to 9.4 %;
- the share of gas oil (including diesel, not heating oil) has increased from 17.7 % to 31 %;
- the share of gasoline has decreased from 22.7 % to 16.1 %;
- the share of heavy fuel oil has decreased from 16.3 % to 6.4 %.

At the time of writing, the EU production-consumption gap is still closed via international trade in refined products. The EU imports diesel (mostly from the Russian Federation) and exports gasoline (mostly to the United States of America, and to a lesser extent, to Africa and the Middle East). As Figure 1.6 shows, this import-export EU market was almost balanced in 2005.

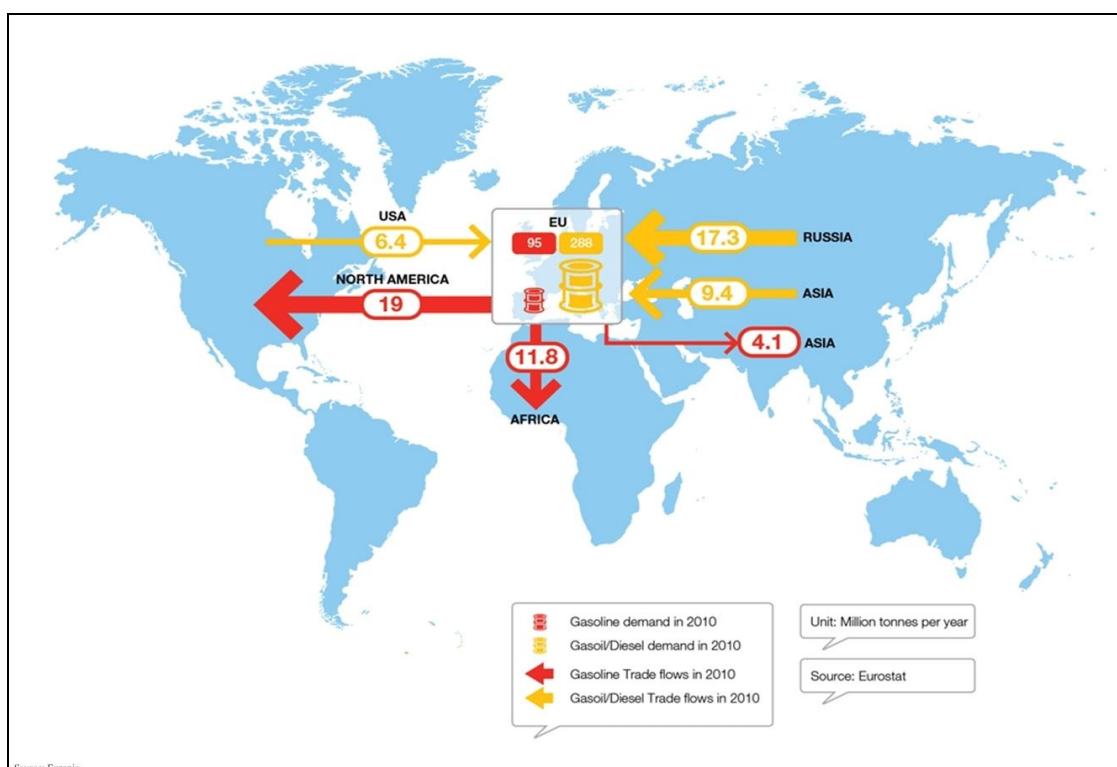


Figure 1.6: Major gasoline and diesel trade to and from the EU

However, the US, and the Middle Eastern and Asian countries have been increasing their refining capacity. Also, North America is expected to become an important diesel exporter. In Table 1.8, the total imports and exports of petroleum products for the year 2009 by region are given.

Table 1.8: Worldwide import/export of products (2009 – 2012)

| Import/export of oil products Millions of tonnes per year | 2009 | | 2012 | |
|--|-----------------|-----------------|-----------------|-----------------|
| | Product imports | Product exports | Product imports | Product exports |
| US | 122.0 | 89.5 | 100.5 | 127.5 |
| Canada | 15.3 | 25.7 | 10.1 | 29.7 |
| Mexico | 21.0 | 8.0 | 27.9 | 3.7 |
| South and Central America | 41.3 | 54.4 | 67.7 | 33.1 |
| Europe | 152.0 | 72.9 | 142.8 | 85.9 |
| Former Soviet Union | 3.2 | 105.1 | 5.5 | 122.2 |
| Middle East | 10.5 | 91.6 | 26.8 | 98.5 |
| North Africa | 10.0 | 25.3 | 15.0 | 22.3 |
| West Africa | 12.1 | 5.3 | 11.4 | 11.3 |
| East and Southern Africa | 5.7 | 0.3 | 12.5 | 0.7 |
| Australasia | 17.1 | 2.0 | 18.2 | 7.9 |
| China | 49.8 | 29.4 | 83.0 | 25.8 |
| India | 10.4 | 35.4 | 15.5 | 64.7 |
| Japan | 35.3 | 16.5 | 48.2 | 10.6 |
| Singapore | 79.8 | 72.0 | 96.7 | 71.0 |
| Other Asia Pacific | 127.6 | 59.9 | 120.2 | 87.0 |
| Total world | 714 | | 802 | |
| Note: Bunkers are not included as exports. Intra-area movements (e.g. between countries in Europe) are excluded. | | | | |
| Source: [71, BP 2010], [277, BP 2013] | | | | |

As far as the quality of refined products is concerned, the phasing out of lead from gasoline has been completed and new specifications (see Table 1.9) have required a reduction of the sulphur content for all types of automotive fuels, lower aromatics, particularly benzene in gasoline, and reduced polyaromatic hydrocarbons and a higher cetane number in diesel. The trend is that environmental quality requirements will become more stringent for all refinery products. Moreover, EU acidification puts additional pressure on the sulphur content of liquid fuels, and therefore also on the sulphur content of the fuels used in refineries. Meeting these new specifications require additional investment, particularly in desulphurisation capacity, adding more pressure to the restructuring process of the sector.

Table 1.9: Evolution of mineral oil product specifications

| Refinery product | Unit | Product specification | 2000 | 2005 | 2009 |
|---|-------------------|-----------------------|-----------|------------|----------|
| | | Before 2000 | | | |
| Gasoline | | | | | |
| Sulphur | ppm | 500 max. | 150 max. | 50 max. | 10 max. |
| Lead | g/l | 0.15 | 0.005 max | 10 max | 10 max |
| Aromatics | % v/v | none | 42 max. | 35 max. | 35 max. |
| Olefins | % v/v | none | 18 max. | 18 max. | 18 max. |
| Aromatics | % v/v | | 42 max | 35 max | 35 max |
| Benzene | % v/v | 5 max. | 1.0 max. | 1.0 max. | 1.0 max. |
| Evaporation at 100 °C (summer) | % | 65/70 max. | 46 min. | 46 min. | 46 min. |
| Evaporation at 150 °C (winter) | % | none | 75 min. | 75 min. | 75 min. |
| RVP, summer | kPa | 80 | 60 max. | 60 max. | 60 max. |
| Oxygen | % | 2.5 max. | 2.7 max. | 2.7 max. | 3.7 |
| Methanol | % v/v | | 3 | 3 | 3 |
| Ethanol | % v/v | | 5 | 5 | 10 |
| Iso-propyl alcohol | % v/v | | 10 | 10 | 12 |
| Ter-butyl alcohol | % v/v | | 7 | 7 | 15 |
| Iso-butyl alcohol | % v/v | | 10 | 10 | 15 |
| Ethers >C ₄ | % v/v | | 15 | 15 | 22 |
| Other oxygenates | % v/v | | 10 | 10 | 15 |
| Diesel | | | | | |
| Sulphur | ppm | 500 max. | 350 max. | 50 max. | 10 max |
| Cetane number | | 49 min. | 51 min. | 51 min. | 51 min. |
| Density at 15°C | kg/m ³ | 860 max. | 845 max. | 845 max. | 845 max. |
| Distillation 95 % (v/v) | °C | 370 max. | 360 max. | 360 max. | 360 max. |
| Polycyclic Aromatics | % m/m | none | 11 max. | 11 max. | 8 max. |
| FAME - EN 14078 | % v/v | none | none | none | 7 max. |
| Heating gas oil | | | | | |
| Sulphur | % m/m | | | | 2008 |
| Inland heavy fuel oil | | | | | |
| Sulphur | % m/m | | | 2003 | |
| Bunker fuel oil in SO_x emission control zones | | | | | |
| Sulphur | % w/w | | | IMO - 2003 | |
| | | | | 1.5 | |

Directive 2012/33/EU of 21 November 2012 amending Directive 1999/32/EC as regards the sulphur content of marine fuels aims at taking into account the more stringent rules for the sulphur content of fuels used by maritime transport agreed under the International Maritime Organisation (IMO) through the revised Annex VI to the MARPOL Convention.

It introduces, in particular, stricter sulphur limits for marine fuel:

- in Sulphur Emission Control Areas (SECAs): 1 % as of 1 July 2010 and 0.10 % as of 1 January 2015;
- in sea areas outside SECAs: 3.5 % as of 1 January 2012 and 0.50 % from either 1 January 2020 or 2025 (to be decided in 2018).

1.2.4.2 Natural gas

In 2007, the world's largest exporter of natural gas by far was Russia (around 200 billion m³/yr), followed by Canada and Norway with around 87 billion m³/yr. The first EU-27 exporter, the Netherlands, ranked in ninth place with 30 billion m³/yr.

Table 1.10 gives the imports of natural gas by region for the year 2009.

Table 1.10: Natural gas imports in 2009

| Natural gas imports | Pipeline imports (billion m ³) | LNG imports | Total imports |
|---|--|---------------|---------------|
| North America | 122.49 | 17.33 | 139.82 |
| South and Central America | 12.49 | 3.28 | 15.77 |
| Europe and Eurasia | 443.97 | 69.02 | 512.99 |
| Austria | 7.98 | – | 7.98 |
| Belgium | 15.01 | 6.53 | 21.54 |
| Bulgaria | 2.64 | – | 2.64 |
| Croatia | 1.20 | – | 1.20 |
| Czech Republic | 9.40 | – | 9.40 |
| Estonia | 0.71 | – | 0.71 |
| Finland | 4.10 | – | 4.10 |
| France | 35.99 | 13.07 | 49.06 |
| Germany | 88.82 | – | 88.82 |
| Greece | 2.55 | 0.74 | 3.29 |
| Hungary | 8.10 | – | 8.10 |
| Ireland | 5.08 | – | 5.08 |
| Italy | 66.41 | 2.90 | 69.31 |
| Latvia | 1.19 | – | 1.19 |
| Lithuania | 2.77 | – | 2.77 |
| The Netherlands | 17.21 | – | 17.21 |
| Poland | 9.15 | – | 9.15 |
| Portugal | 1.59 | 2.82 | 4.41 |
| Romania | 2.05 | – | 2.05 |
| Slovakia | 5.40 | – | 5.40 |
| Slovenia | 0.89 | – | 0.89 |
| Spain | 8.99 | 27.01 | 36.00 |
| Sweden | 1.31 | – | 1.31 |
| United Kingdom | 30.88 | 10.24 | 41.12 |
| Rest of Europe and Eurasia | 114.55 | 5.71 | 120.26 |
| Middle East | 30.42 | 0.89 | 31.31 |
| Africa | 5.25 | | 5.25 |
| Asia Pacific | 19.16 | 152.27 | 171.43 |
| Total | 633.77 | 242.77 | 876.54 |
| <i>Source: BP Statistical Review Of World Energy 2010</i> | | | |

Unconventional gas: The use of horizontal drilling in conjunction with hydraulic fracturing has greatly expanded the ability of producers to profitably produce natural gas from low

permeability geological formations, particularly shale formations. Application of fracturing techniques to stimulate oil and gas production began to grow rapidly in the 1950s, although experimentation dates back to the nineteenth century.

Shale gas (see definition below) has become a 'game changer' for the natural gas market. The proliferation of activity into new shale plays has increased dry shale gas production in the United States from 11 billion cubic metres in 2000 to 136 billion in 2010, or 23 % of US dry gas production. Wet shale gas reserves have increased to about 1 700 billion cubic metres by year-end 2009, when they comprised about 21 % of overall US natural gas reserves, now at the highest level since 1971.

Thus, adding the identified shale gas resources to other gas resources increases total world technically recoverable gas resources by over 40 % to 640 000 billion cubic metres.

Shale gas is extracted by fracking techniques that involve high-pressure injection of water, sand and chemical additives, and thus environmental impacts need to be taken into consideration. Some useful definitions about these new techniques are provided:

- Shale gas - Natural gas stored in extremely small pore spaces or bonded to organic material within rock composed mostly of consolidated clay and siltstone.
- Tight gas - Natural gas stored in small pore spaces in very low permeability underground formations, such as sandstone, siltstone or limestone.
- Deep gas - Unconventional natural gas that is located deep within geological formations.
- Coalbed methane (CBM) - Natural gas stored in naturally occurring fracture systems or bonded onto coal. A liquid, low-pressure sweet gas, CBM gas is used to fuel hot water heaters, furnaces and ranges.

Midsized companies lead this extraction activity: e.g. Chesapeake, Exco, XTO Energy, Atlas, Encana or Duvenay.

Table 1.11: Estimated technically recoverable shale gas resources in 32 countries

| Country | Estimated technically recoverable reserves (billion m ³) |
|---|---|
| China | 36 104 |
| United States | 24 409 |
| Argentina | 21 917 |
| Mexico | 19 284 |
| South Africa | 13 734 |
| Australia | 11 214 |
| Canada | 10 987 |
| Libya | 8 212 |
| Algeria | 6 541 |
| Brazil | 6 400 |
| <i>Poland</i> | 5 295 |
| <i>France</i> | 5 097 |
| Norway | 2 350 |
| Chile | 1 812 |
| India | 1 784 |
| Paraguay | 1 756 |
| Pakistan | 1 444 |
| Bolivia | 1 359 |
| Ukraine | 1 189 |
| <i>Sweden</i> | 1 161 |
| <i>Denmark</i> | 651 |
| Uruguay | 595 |
| <i>United Kingdom</i> | 566 |
| Colombia | 538 |
| Tunisia | 510 |
| <i>Netherlands</i> | 481 |
| Turkey | 425 |
| Morocco | 311 |
| Venezuela | 311 |
| <i>Germany</i> | 227 |
| Western Sahara | 198 |
| <i>Lithuania</i> | 113 |
| Total | 186 977 |
| NB: <i>Italics: EU-27 Member States</i> | |
| Source: [73, US DOE 2011] | |

1.3 European refineries

1.3.1 Oil refineries

At the time of writing (2013), there are close to 120 crude oil refineries spread around the EU+ countries. Of these refineries, about ten are specialist refineries producing mainly lubricating oil basestocks or bitumen.

Figure 1.7 and the associated table show the distribution of European refineries by country. As can be seen on the map, refineries are mainly placed close to the sea or to a big river, to satisfy their need for large amounts of cooling water, as well as to facilitate the sea transport of raw materials and products. There are some places in Europe with a high concentration of refineries (e.g. Rotterdam in the Netherlands; Antwerp in Belgium and Sicily in Italy).

As a result of overcapacity in the European refinery sector, very few new oil refineries have been built in the last 35 years. In fact, only 9 % of the existing refineries have been built in this period and only 2 % before 2000, 95 % being built before 1981 and 44 % before 1961 (see Table 1.12). Although most refineries will have had upgrades and new units built since they were first commissioned, their overall structure, and in particular items like the pattern of sewer systems, will have remained essentially unchanged.

Table 1.12: Percentage of refineries built during different time periods in the EU-27

| Time period | Number of refineries built in the time period | Percentage of refineries built during the time period (%) | Cumulative percentage |
|-------------|---|---|-----------------------|
| Before 1900 | 1 | 1 | 1 |
| 1900 – 1910 | 2 | 2 | 3 |
| 1911 – 1920 | 1 | 1 | 4 |
| 1921 – 1930 | 9 | 9 | 13 |
| 1931 – 1940 | 7 | 7 | 19 |
| 1941 – 1950 | 8 | 8 | 27 |
| 1951 – 1960 | 17 | 17 | 44 |
| 1961 – 1970 | 41 | 40 | 83 |
| 1971 – 1980 | 12 | 12 | 95 |
| 1981 – 1990 | 3 | 3 | 98 |
| 1991 - 2000 | 2 | 2 | 100 |
| 2000 - 2010 | 0 | 0 | 100 |
| Total | 103 (*) | | |

(*) Refinery in Martinique not included within the table. Some refineries have been demolished recently.
Source: CONCAWE

1.3.2 Gas refineries

Seventeen onshore natural gas plants have been identified in Europe. Three have been identified in the Netherlands, six in Norway, including LNG plants, and nine in the United Kingdom.

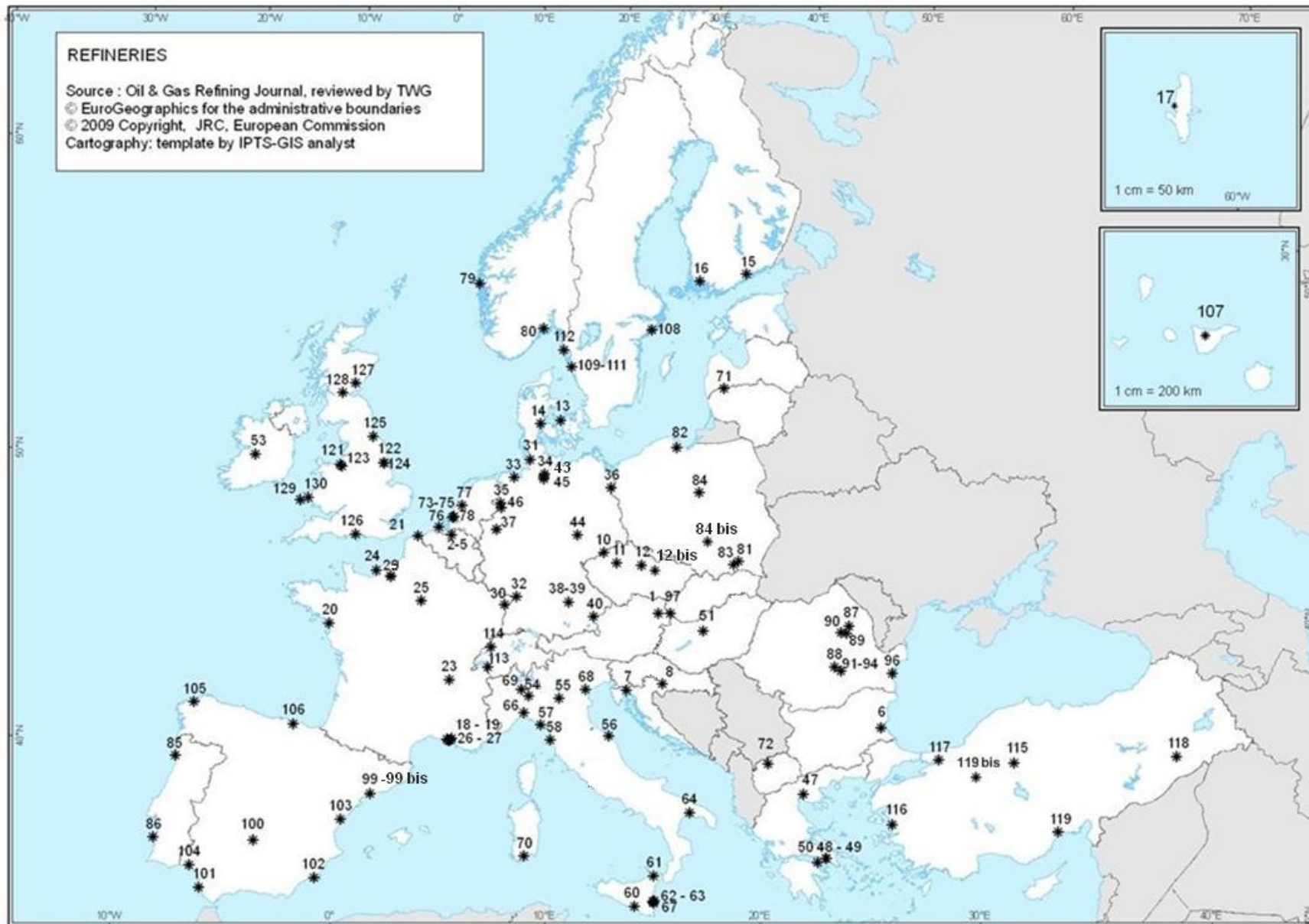


Figure 1.7: Geographical distribution of the European refineries

| ID | Country | Refinery location | ID | Country | Refinery location | ID | Country | Refinery location |
|---------|-----------------------------|----------------------|----------|------------------------|--------------------------|-----------------|----------------------|--------------------------|
| 1 | Austria | Schwechat | 51 | Hungary | Szazhalombatta | 97 | Slovakia | Bratislava |
| 2 – 5 | Belgium | Antwerpen | 53 | Ireland | Whitegate | 99-99bis | | Tarragona |
| 6 | Bulgaria | Burgas | 54 | | Sannazzaro, Pavia | 100 | | Puertollano, Ciudad Real |
| 7 | Croatia | Rijeka | 55 | | Mantova | 101 | | Cadiz |
| 8 | | Sisak | 56 | | Falconara, Marittima | 102 | | Cartagena, Murcia |
| | | | 57 | | Ravenna | 103 | | Castellon de la Plana |
| 10 | Czech Republic | Litvinov | 58 | | Livorno | 104 | | Huelva |
| 11 | | Kralupy | 60 | | Gela, Ragusa | 105 | | La Coruña |
| 12 | | Pardubice | 61 | | Milazzo, Messina | 106 | | Muskiz Vizcaya |
| 12bis | | Kolin | 62 | | Priolo, Sicily | 107 | | Tenerife |
| 13 | Denmark | Kalundborg | 63 | Italy | Augusta, Siracusa | 108 | Sweden | Nynashamn |
| 14 | | Fredericia | 64 | | Taranto | 109 – 111 | | Gothenburg |
| 15 | Finland | Porvoo | 66 | | Busalla | 112 | Switzerland | Brofjorden - Lysekil |
| 16 | | Naantali | 67 | | Melilli, Sicily | 113 | | Collombey |
| 17 | France | Fort-de-France | 68 | | Porto Marghera | 114 | Turkey | Cressier |
| 18 | | Fos-sur-Mer | 69 | | S. Martino Di Trecate S. | 115 | | Kirikkale |
| 19 | | Berre l'Etang * | 70 | | Sarroch | 116 | | Aliaga - Izmir |
| 20 | | Donges | | | | 117 | | Izmit |
| 21 | | Dunkerque | | | | 118 | | Batman, Siirt |
| 23 | | Feyzin | 71 | | Lithuania | Mazeikiai | 119 | Mersin |
| 24 | | Gonfreville L'orcher | 72 | FYROM | Skopje | 119 bis | Narli, Kahramanmaras | |
| 25 | | Grandpuits | 73 – 75 | | Rotterdam | 121 | United Kingdom | Eastham |
| 26 | | La Mede | 76 | The Netherlands | Vlissingen | 122 | | South Killingholme |
| 27 | | Lavera | 78 | | Pernis | 123 | | Stanlow |
| 29 | | Port Jérôme | 79 | Norway | Mongstad | 124 | | South Killingholme |
| 31 | Heide | 80 | Slagen | | 126 | Fawley | | |
| 32 | Karlsruhe | 81 | Poland | Jaslo | 127 | Dundee | | |
| | | 82 | | Gdansk | 128 | Grangemouth | | |
| 34 | Hamburg | 83 | | Gorlice | 129 | Milford Haven | | |
| 35 | Lingen | 84 | Plock | 130 | Pembroke, Dyfed | | | |
| 36 | Schwedt | 84 bis | Trzebina | | | | | |
| 37 | Gelsenkirchen | 85 | Portugal | Leca Da Palmeira Porto | | | | |
| 38 - 39 | Vohburg/Ingolstadt/Neustadt | 86 | | Sines | | | | |
| 40 | Burghausen | 87 | Romania | Bacau | | | | |
| 43 | Harburg | 88 | | Campina | | | | |
| 44 | Leuna, Spergau | 89 | | Onesti, Bacau | | | | |
| 45 | Rheinland | 90 | | Darmanesti | | | | |
| 46 | Salzbergen | 91 – 94 | | Ploiesti | | | | |
| 47 | Greece | Thessaloniki | 96 | Midia | | | | |
| 48 | | Elefsis | | | | | | |
| 49 | | Aspropyrgos | | | | | | |
| 50 | | Ahghii Theodori | | | | | | |

NB: *In italics*: lubricant and bitumen specialised refineries
* Refinery under 'mothballing' in 2013
Source: [132, O&Gas Journal 2011] reviewed by TWG, 2013

1.3.3 Technical characteristics of European refineries

Compared to other parts of the world, refining configurations of western European refineries reflect to some extent their technical adaptation to the local demands of middle distillates, in particular diesel and jet fuel: they show proportionally more hydrotreating and hydrocracking capacities and less catalytic cracking capacities than in North America. As shown in Table 1.13, the most complex refinery configurations are observed in North American refineries. As a result, they produce three times less heavy residues than in Europe, and six times less than in the Russian Federation or in Africa.

Table 1.13: Refining configurations as a percentage of crude distillation

| World regions | Catalytic cracking | Catalytic reforming | Catalytic hydrocracking | Catalytic hydrotreating |
|----------------|--------------------|---------------------|-------------------------|-------------------------|
| Africa | 6.5 | 14.7 | 1.9 | 28.0 |
| Asia | 11.9 | 8.7 | 3.3 | 38.5 |
| Eastern Europe | 9.0 | 14.5 | 3.1 | 41.6 |
| Middle East | 5.1 | 9.2 | 8.3 | 29.2 |
| North America | 20.2 | 31.9 | 8.4 | 73.4 |
| South America | 19.6 | 6.4 | 2.1 | 28.9 |
| Western Europe | 15.0 | 14.3 | 7.0 | 66.7 |

Source: [20, Gary et al.2007]

Table 1.14 shows the number of processes currently operating in the mineral oil refineries in each country. As can be seen, crude and vacuum distillations, catalytic hydrotreatment and catalytic reforming are the most common processes, as they are found in the simplest of refineries. It may be surprising that the number of catalytic hydrotreatment processes is higher than the number of refineries, but the reason is simply that there is, on average, more than one catalytic hydrotreatment in each European refinery. The least common processes in European refineries are coking and polymerisation/dimerisation.

Some of these refining processes have been analysed in order to determine the type of technique or techniques used to perform a certain process. For instance, there are currently two technologies to carry out alkylation, namely sulphuric and hydrofluoric. In this case, these two technologies are competitors but in other cases, such as hydrotreating, one technique does not exclude another. As can be seen in Table 1.14, some techniques are really predominant in particular processes in European refineries. This category includes delayed coking, visbreaking, fluid catalytic cracking, hydrofluoric alkylation, C₅ and C₆ isomerisation, Methyl tert-butyl ether (MTBE) production and steam reforming for the production of hydrogen. Other processes where one technique is less predominant are catalytic reforming, catalytic hydrorefining, catalytic hydrotreating and hydrogen recovery process.

Table 1.14: Number of type of processes per country

| | Process | | EU-27 number | EU+ number | World M barrel/day |
|-----------|--------------------------------|--|-----------------|---------------|-----------------------|
| | | | | | |
| | 1 | Fluid coking | 2 | 2 | |
| | 2 | Delayed coking | 13 | 15 | |
| | 3 | Other | 1 | 1 | |
| 7 | Coking | | 16 | 16 | 4.61 |
| | 1 | Thermal cracking | 14 | 16 | |
| | 2 | Visbreaking | 52 | 57 | |
| 22 | Thermal ops | | 66 | 66 | 3.82 |
| | 1 | Fluid | 58 | 64 | |
| | 1 | Other | 3 | 4 | |
| 5 | Catalytic cracking | | 61 | 61 | 14.66 |
| | 1 | Semi-regenerative | 58 | 71 | |
| | 2 | Cyclic | 13 | 13 | |
| | 3 | Continuous regenerative | 34 | 36 | |
| | 4 | Other | 0 | 0 | |
| 6 | Catalytic reforming | | 105 | 105 | 11.51 |
| | 1 | Distillate upgrading | 24 | 27 | |
| | 2 | Residual upgrading | 6 | 7 | |
| | 3 | Lube oil manufacturing | 5 | 5 | |
| | 4 | Other | 3 | 3 | |
| | c | Conventional | 15 | 17 | |
| | m | Mild to moderate | 8 | 8 | |
| 13 | Catalytic hydrocracking | | 38 | 38 | 5.41 |
| | 1 | Pretreatment of catalytic reformer feeds | 81 | 87 | |
| | 2 | Other naphtha desulphurisation | 26 | 26 | |
| | 3 | Naphtha aromatics saturation | 11 | 11 | |
| | 4 | Kerosene/jet desulphurisation | 35 | 35 | |
| | 5 | Diesel desulphurisation | 65 | 70 | |
| | 6 | Distillate aromatics saturation | 3 | 3 | |
| | 7 | Other distillates | 10 | 10 | |
| | 8 | Pretreatment cat. crackers feed | 20 | 20 | |
| | 9 | Other heavy GO | 13 | 14 | |
| | 10 | Residue hydrotreating | 2 | 2 | |
| | 11 | Lube oil polishing | 15 | 15 | |
| | 12 | Post hydrotreating of FCC naphtha | 19 | 20 | |
| | 13 | Other | 9 | 9 | |
| 13 | Catalytic hydrotreating | | 309 | 309 | 45.43 |

| | Process | | EU-27 number | EU+ number | World M barrel/day |
|-----------|------------------------------------|-----------------------------------|-----------------|---------------|--------------------------|
| | | | | | |
| 19 | Crude | | 110 | 124 | 88.22 |
| 19 | Vacuum | | 101 | 110 | 29.18 |
| | 1 | Sulphuric acid | 7 | 7 | |
| | 2 | Hydrofluoric acid | 30 | 30 | |
| 2 | Alkylation | | 37 | 37 | 2.06 |
| | 1 | Polymerisation | 11 | 13 | |
| | 2 | Dimerisation | 0 | 0 | |
| 18 | Polymerisation/dimerisation | | 11 | 13 | 0.2 |
| | 1 | BTX | 21 | 22 | |
| | 2 | Hydrodealkylation | 5 | 5 | |
| | 3 | Cyclohexane | 5 | 5 | |
| | 4 | Cumene | 3 | 3 | |
| | Aromatics | | 34 | 34 | 1.34 |
| | 1 | C ₄ | 8 | 8 | |
| | 2 | C ₅ | 8 | 8 | |
| | 3 | C ₅ and C ₆ | 124 | 131 | |
| 16 | Isomerisation | | 140 | 140 | 1.7 |
| | 1 | MTBE | 22 | 22 | |
| | 2 | ETBE | 12 | 12 | |
| | 3 | TAME | 4 | 4 | |
| | 4 | Other | 1 | 1 | |
| 11 | Oxygenates | | 39 | 39 | 0.19 |
| | 1 | Steam methane Reforming | 33 | 34 | |
| | 2 | Steam naphtha Reforming | 9 | 11 | |
| | 3 | Partial oxidation | 5 | 5 | |
| | 4 | Pressure swing adsorption | 22 | 25 | |
| | 5 | Cryogenic | 7 | 7 | |
| | 6 | Membrane | 6 | 7 | |
| | 7 | Other | 2 | 2 | |
| 14 | Hydrogen production | | 84 | 84 | 0.02 |
| 3 | Lubes | | 32 | 34 | 0.79 |
| 7 | Coke | | 17 | 20 | 0.2 |
| 23 | Sulphur | | 77 | 83 | 0.08 |
| 4 | Asphalt | | 57 | 63 | 1.77 |

Source: [70, Oil & Gas 2010]

Following the analysis of the type of processes, Figure 1.8 shows the capacity ranges for the different processes found in European refineries, both in thousands of barrels and as a percentage of the worldwide refinery base. As can be seen, the ranges are quite large, explaining again the diversity of type of refineries found in Europe. For instance, there exist huge differences in the capacity of crude units or catalytic hydrotreating. Smaller differences exist in the coking processes and alkylation processes.

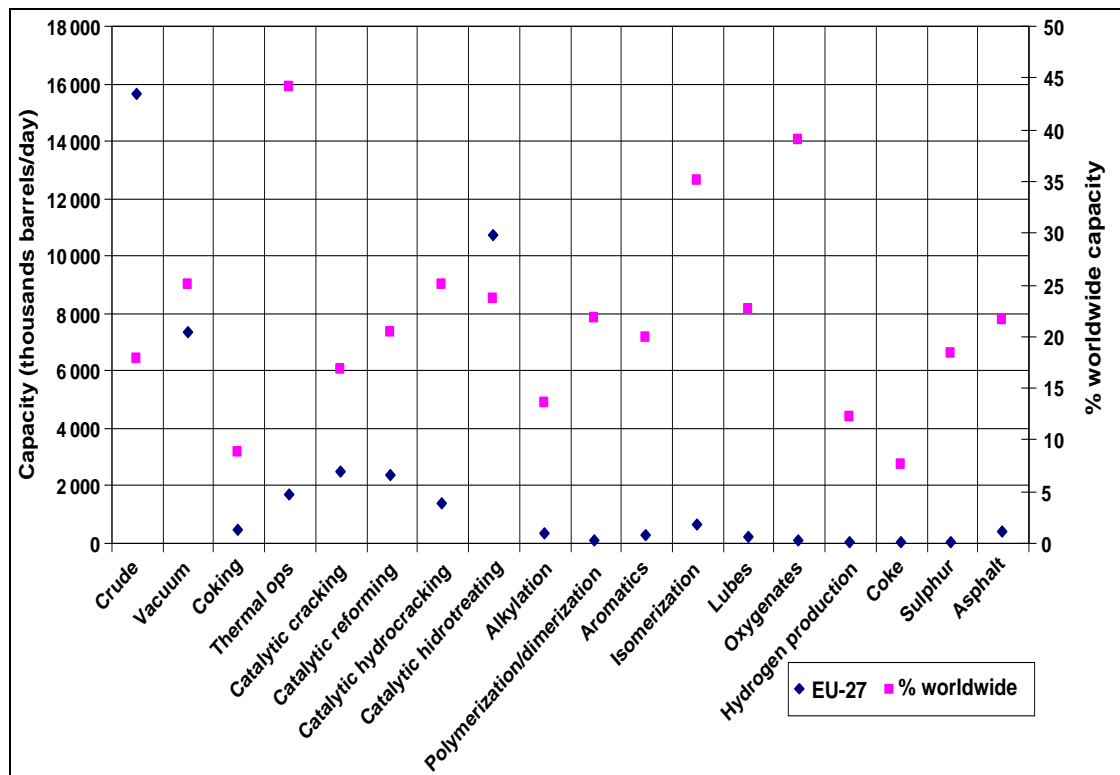


Figure 1.8: Capacity of the various processes in the EU-27 refineries (O&GJ 2011)

There are various approaches to defining a refinery complexity. In some studies it is common to distinguish between several types of refinery configuration according to complexity (see Annex 8.1). The Nelson refinery complexity index was used for the construction of Figure 1.9. This classification is to define five different types of configuration. Other definitions are used in the industry, such as Equivalent Distillation Capacity as used by Solomon Associates.

Figure 1.9 tries to illustrate the variety of complexity of refineries within Europe. The Y-axis represents refinery complexity calculated according to the Nelson refinery complexity index [216, Johnston 1996]⁽²⁾. The X-axis represents the different EU+ countries. If the Y gap of the EU+ refineries is divided into four categories (less than 3.9, between 3.9 and less than 6.1, between 6.1 and 8.4 and more than 8.4⁽³⁾), it can be seen that 18 % of the refineries belong to the lowest category, 30 % belong to the second category, 41 % to the third and 11 % to the group of more complex refineries. Consequently, seven out of 10 refineries of the EU+ can be considered as refineries with medium complexity.

Even if there are still a number of hydroskimming refineries in operation, the most common configuration in the EU+ is the catalytic cracker configuration.

⁽²⁾ Nelson developed a system to quantify the relative cost of components that make up a refinery. It is a pure cost index that provides a relative measure of the construction costs of a particular refinery based on its crude and upgrading capacity. Nelson assigned a factor of 1 to the distillation unit. All other units are rated in terms of their cost relative to this unit.

⁽³⁾ Limits of the categories calculated as average \pm standard deviation.

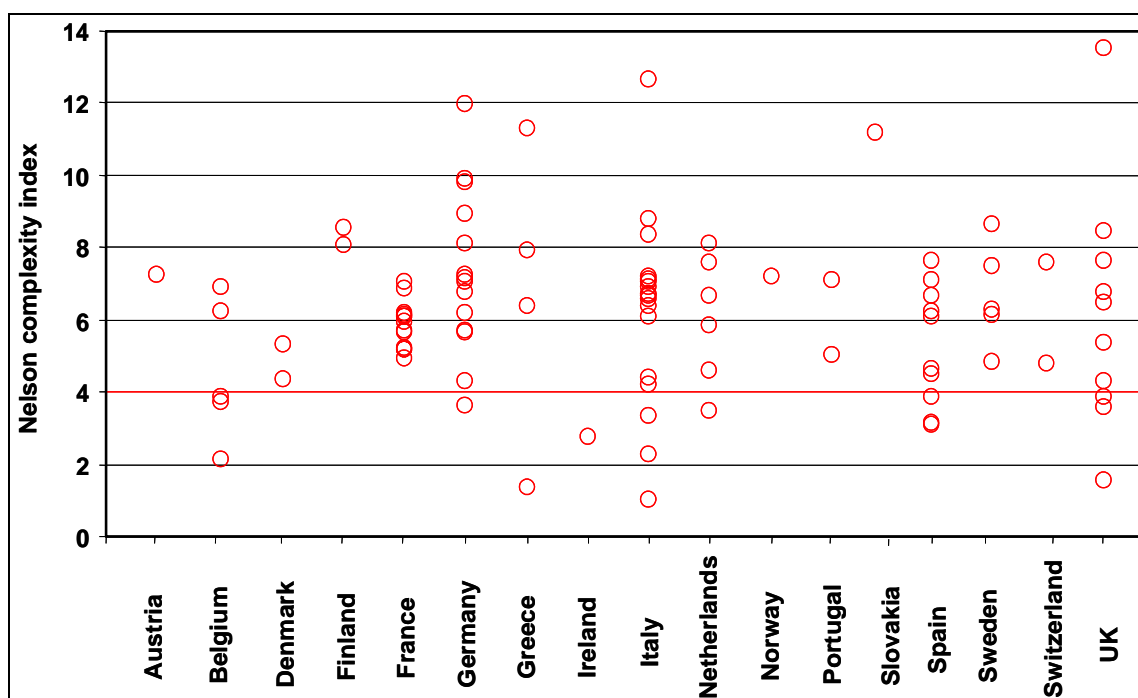


Figure 1.9: Nelson complexity index dispersion for some European refineries per country

Figure 1.10 shows the distribution of the refineries in the EU+ according to their complexity (NCI: Nelson complexity index) in 2005 and 2009 [112, CONCAWE 2011].

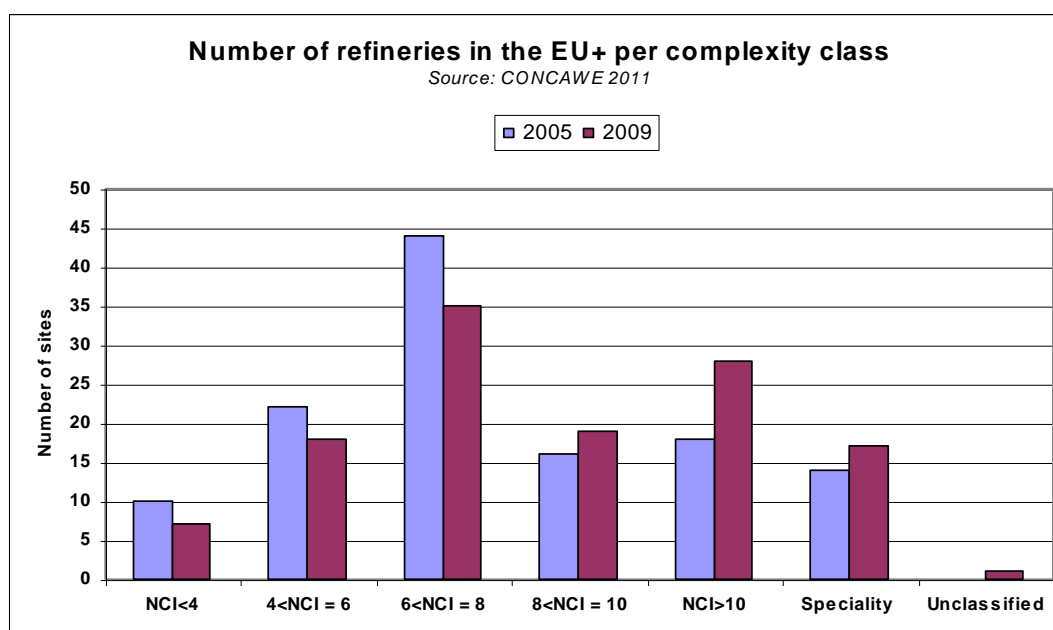


Figure 1.10: Distribution of refineries in the EU+ according to the Nelson complexity index

1.3.4 Employment in the European refinery sector

According to Eurostat (Manufacture of refined petroleum products -NACE Rev.2 group 19.2), in 2010, the European refining industry employed about 123 000 people in the EU. In addition, it can be considered that as many as 400 000 to 600 000 jobs are directly dependent on the EU refining industry. [72, COM 2010]

1.4 Main environmental issues in the refining sector

Refineries are industrial sites that manage huge amounts of raw materials and products, and they are also intensive consumers of energy and water used to carry out the processes. In their storage and refining processes, refineries generate emissions to the atmosphere, to water and to the soil. Environmental management has become a major factor for refineries. The refining industry is a mature industry, and pollution abatement programmes have been carried out in most refineries for a long time to different extents. As a result, the emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.

It is important to know, with respect to the quality and quantity of refinery emissions, that on a macro scale the crude oils vary only to a limited extent in their composition. Moreover, refineries are often limited to a comparatively narrow range of crude oil diets. Normally, when switching from one crude oil to another within this range, large variations in refinery emissions are not expected. Consequently the type and quantity of refinery emissions to the environment are well-known during normal operations. However, from time to time, processing of crude oils previously unknown to the refinery can have unforeseen impacts on the performance of refinery processes; leading to an increase in emissions. This is particularly likely to affect water emissions and to a lesser extent air emissions.

1.4.1 Emissions to the atmosphere

According to available European emission inventories [35, EEA 2009], oil refining is responsible for a significant contribution to air emissions generated by industrial activities. In the particular case of sulphur oxides, this contribution is significant (around 7 %) even when observed at the level of the overall emissions by all human activities.

Table 1.15 gives an estimation of the contribution of oil and gas refineries with regard to emissions reported in 2007 and 2009 in the European Union for some main parameters.

Table 1.15: Contribution of oil refining to the EU-27 air emissions (2007 – 2009)

| Main air pollutants | Overall emissions from industrial activities (kt) | Emissions from the energy production and use ⁽¹⁾ (kt) | Oil refining emissions 2007 ⁽²⁾ (kt) (#sites) | Part of oil refining emissions from the energy production and use (%) | Part of all emissions from all industrial activities (%) | Oil refining emissions 2009 ⁽²⁾ (kt) (#sites) |
|--|---|--|--|---|--|--|
| Greenhouse gases (CO ₂ -equivalent) | 4 638 000 | 2 201 000 | 158 880 (105) | 7.2 | 3.4 | 146 745 (100) |
| Carbon monoxide (CO) | 27 921 | 4 634 | 58 (27) | 1.3 | 0.2 | 55 (27) |
| Fine particulates (PM ₁₀) | 1 952 | 312 | 8 (44) | 2.6 | 0.4 | 7 (40) |
| Fine particulates (PM _{2.5}) | 1 266 | 224 | 11 | 4.9 | 0.9 | - |
| Nitrogen oxides (NO _x) | 10 939 | 3 991 | 193 (110) | 4.8 | 1.8 | 162 (105) |
| Sulphur oxides (SO _x) | 7 442 | 6 024 | 574 (111) | 9.5 | 7.7 | 426 (103) |
| Volatile organic compounds (NMVOC) | 8 951 | 265 | 180 (98) | 67.9 | 2.0 | 138 (93) |

⁽¹⁾ This sector covers the production of energy from fossil fuels for power and heat generation and industrial manufacturing (NFR Sectors 1A1 and 1A2).
⁽²⁾ Figures given for NFR Sector 1A1b.
Source: E-PRTR data

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NO_x), particulates, and sulphur oxides (SO_x) to the atmosphere.

Refinery processes require a lot of energy; typically more than 60 % of refinery air emissions are related to the production of energy for the various processes.

Sulphur recovery units and flares also contribute to these emissions. Catalyst changeovers and cokers release particulates. Volatile organic compounds (VOCs) are released from storage, product loading and handling facilities, oil/water separation systems and, as fugitive emissions, from flanges, valves, seals and drains. Other emissions to the atmosphere are H₂S, NH₃, BTX, CS₂, COS, HF and metals as constituents of the particulates (V, Ni and others). Table 1.16 shows a very brief summary of the main pollutants emitted by a typical refinery, with their main sources.

Table 1.16: Main air pollutants and their main sources emitted by refineries

| Main air pollutants | Main sources |
|---|--|
| Carbon dioxide | Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Flare systems Incinerators LNG plant CO ₂ separation |
| Carbon monoxide | Process furnaces and boilers Fluidised catalytic cracking regenerators CO boilers Sulphur recovery units Flare systems Incinerators |
| Nitrogen oxides (NO, NO ₂) | Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Incinerators Flare systems |
| Nitrous oxide (N ₂ O) | Fluidised catalytic cracking regenerators |
| Particulates (including metals) | Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators CO boilers Coke plants Incinerators |
| Sulphur oxides | Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Sulphur recovery units (SRU) Flare system Incinerators |
| Volatile organic compounds (VOCs) | Storage and handling facilities Gas separation units Oil/water separation systems Fugitive emissions (valves, flanges, etc.) Vents Flare systems |

Carbon dioxide (CO₂) is the greenhouse gas which receives the most attention in the debate about global climate change. The main source of CO₂ emissions is the production of energy. Since the first oil crisis in 1973, refineries have made a concerted effort to enhance energy efficiency. Despite these energy conservation measures, refinery energy demand has increased due to tightened product specifications and a shift over the years from producing heavy fuel oils to transport fuels. The fuel used for petroleum refining increased by about 15 % in the EU-27 between 1990 and 2007, which represents the third largest key source increase during this period, after road transportation, public electricity and heat production. Even if gaseous fuels use has more than doubled since 1990, liquid fuels still represented in 2007 over 90 % of all fuel used. The Netherlands and Italy are, with respectively 5 % and 4.5 %, the two Member States with the highest relative importance of CO₂ emissions from petroleum refining in their total greenhouse gas emissions.

Carbon monoxide (CO) always appears as an intermediate product of the combustion processes, in particular in understoichiometric combustion conditions. However, the relevance of CO releases from refineries is not very high compared to CO₂.

Oxides of nitrogen (NO_x), when emitted to the air, can combine with water and form a component of 'acid rain'. Further, NO_x in combination with volatile organic compounds and sunlight can lead to the formation of ground-level ozone. The source of NO_x is mainly the combustion processes; during the combustion of fuel, nitrogen (mainly originating from the combustion air itself) is transformed to a mixture of NO₂ and NO. Combustion conditions play an important role here. N₂O (laughing gas) is a powerful greenhouse gas that contributes to the stratospheric ozone depletion.

Particulate emissions (PM) have become a focus of attention because of their potential adverse health effects, in particular for the smallest particulate matter with an aerodynamic diameter <10 μm (PM₁₀ - EN12341) and <2.5 μm (PM_{2.5} - EN14907). Particulate emissions are caused by the combustion of fuel oils, especially when there is suboptimal combustion. Another significant source is the catalytic cracker. The particulate content of hazardous compounds (e.g. heavy metals and polycyclic aromatic hydrocarbons) is of primary interest in a refining context.

Sulphur oxides (SO_x), when emitted to the air, can combine with water and form a component of 'acid rain'. The main source of SO_x is the production of energy; during combustion, the sulphur in the fuel is transformed to a mixture of SO₂ and SO₃. Another source, typically smaller, is the flue-gas from the sulphur recovery units. There is a direct relation between the sulphur in the feed to a combustion process and the sulphur oxides in its flue-gas. Generally speaking, the sulphur content of the refinery fuel pool is a careful balance between energy required, the type of crude processed, the emission limits and economic optimisations.

Volatile organic compounds (VOCs), as mentioned above, can react with NO_x in the presence of sunlight to form low-level atmospheric ozone. Furthermore, the emission of VOCs can give rise to odour problems, which may result in complaints from nearby residents. The source of VOC emissions is the evaporation and leakage of hydrocarbon fractions potentially associated with all refining activities, e.g. fugitive emissions from pressurised equipment in process units, storage and distribution losses, and waste water treatment evaporation. Hydrocarbons may also be emitted during non-optimal combustion conditions, but these are only a small contribution.

1.4.2 Emissions to water

Petroleum refineries consume water on a continuous basis to maintain the water balances in the steam, cooling water, utility service water, and emergency fire water supply circuits. Water is also consumed for process and maintenance use purposes.

The losses from the steam and cooling water circuits include, but are not limited to:

- condensate purge;
- consumed steam;
- evaporation;
- cooling water purge, and circuit leaks.

The losses from the emergency fire water supply circuits may include scheduled maintenance purges, water used to test and/or utilise emergency firefighting equipment, and circuit leaks. Some of the consumed steam that is input into processing systems comes into direct contact with various fractions of hydrocarbons and substances. The condensates resulting from these uses are separated and extracted from the processing system. Condensates may be collected and processed through a steam stripper to separate and extract hydrogen sulphide (H₂S) and ammonia (NH₃) from the water. The stripped water may then be used for other refining processes, such as crude desalting or water washing of process streams.

The water used for process purposes such as crude desalting or water washing will come into direct contact with either crude oil or other various fractions of hydrocarbons and substances. Wash water and/or steam used to clean and purge systems for maintenance activities can also generate waste water that has been in direct contact with these substances.

Other sources of waste water include, but are not limited to:

- water separated and removed from crude oil, intermediate, and product tanks;
- storm water, utility service water, steam condensate and/or emergency firefighting water that comes into contact with crude oil, intermediates, products, additives, chemicals, and/or lubricating oils in the drainage area;
- water originating from ballast water tanks of vessels offloading or loading petroleum-based materials;
- routine and/or special waste solid-liquid separation activities;
- routine and/or special groundwater extraction activities;
- water discarded from periodic tank and piping system hydro test and metal passivation activities;
- water for sanitary usage.

Rainwater falling onto the site can also come into contact with crude oil and various fractions of hydrocarbons and substances due to entry into some tank systems, secondary containment systems, loading and offloading areas for trucks, railcars, and vessels, production areas that include equipment containing these substances and maintenance work areas.

Rainwater falling onto some non-process areas of the site may have a relatively low risk of coming into contact with materials and substances and therefore may not require treatment prior to discharge into the environment.

A refinery site, therefore, generates a collective mix of waste water streams containing insoluble and soluble substances which become pollutants when released.

Waste water treatment techniques are therefore applied to control the amounts of these pollutants. Treatment techniques are typically directed at reducing the amount of pollutants and the oxygen demand exerted by the waste water before it is released.

The main pollutant parameters include:

- total hydrocarbon content (THC);
- Total Petroleum Hydrocarbon index (TPH index)
- biochemical oxygen demand (BOD);
- chemical oxygen demand (COD) or total organic carbon (TOC);
- ammoniacal nitrogen, total nitrogen;

- total suspended solids (TSS);
- total metals.

Other pollutant parameters include:

- cyanides;
- fluorides phenols;
- phosphates;
- specific metals such as Cd, Ni, Hg, Pb and vanadium;
- benzene;
- toluene, ethylbenzene and xylene (TEX);
- sulphides and other micro-pollutants.

Table 1.17 provides a summary of some of the main water pollutants and their sources within a refinery.

Table 1.17: Main water pollutants (parameters) generated by refineries

| Water pollutant | Source |
|---|--|
| Oil | Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain) |
| H ₂ S (RSH) | Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic |
| NH ₃ (NH ₄ ⁺) | Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, sanitary blocks |
| Phenols | Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water |
| Organic chemicals (BOD, COD, TOC) | Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary blocks |
| CN ⁻ , (CNS ⁻) | Visbreaker, catalytic cracking, spent caustic, ballast water |
| TSS | Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary blocks |
| Amines compounds | CO ₂ removal in LNG plants |
| <i>Source: [166, CONCAWE 1999]</i> | |

Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted to prevention and reduction of contaminated waste water streams to the final treatment units.

Table 1.18: Evolution of some water pollutants released from refineries

| E-PRTR data | Tonnes/ year | Number of sites | Tonnes/ year | Number of sites | Tonnes/ year | Number of sites |
|---------------------------------|-----------------|--------------------|-----------------|--------------------|-----------------|--------------------|
| | 2004 | | 2007 | | 2009 | |
| TOC | 6475 | 42 | 7951 | 42 | 6074 | 41 |
| Phenols | 45 | 56 | 59 | 59 | 42 | 59 |
| Total Nitrogen | 2769 | 25 | 2245 | 20 | 2103 | 21 |
| Total Phosphorus | 133 | 10 | 201 | 12 | 99 | 11 |
| <i>Source: [74, EEA 2010]</i> | | | | | | |

1.4.3 Waste generation

The amount of waste generated by refineries is small if it is compared to the amount of raw materials and products that they process. Table 1.20 shows the generation and different waste routes according to the European Pollutant Release and Transfer Register (E-PRTR) declarations.

Oil refinery waste normally covers three categories of materials:

- sludges, both oily (e.g. from tank bottoms) and non-oily (e.g. from waste water treatment facilities);
- other refinery wastes, including miscellaneous liquid, semi-liquid or solid wastes (e.g. contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash, spent caustic, spent clay, spent chemicals, acid tar) and;
- non-refining wastes, e.g. domestic, demolition and construction.

Table 1.19 shows a summary of the main types of solid wastes generated in a refinery and their sources.

Table 1.19: Main solid wastes generated by refineries

| Type of waste | Category | Source |
|-------------------------------------|--|--|
| Oiled materials | Oily sludges | Tank bottoms, biotreatment sludges, interceptor sludges, waste water treatment sludges, contaminated soils, desalter sludges |
| | Solid materials | Contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon |
| Non-oiled materials | Spent catalyst (excluding precious metals) | Fluid catalytic cracking unit catalyst, hydrodesulphurisation/hydrotreatment catalyst, polymerisation unit catalyst, residue conversion catalyst |
| | Other materials | Resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes |
| Drums and containers | | Metal, glass, plastic, paint |
| Radioactive waste (if used) | | Catalysts, laboratory waste |
| Scales | | Leaded/unleaded scales, rust |
| Construction/demolition debris | | Scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood |
| Spent chemicals | | Laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/diethanol amine), TML/TEL (tetra methyl/ethyl lead) |
| Pyrophoric wastes | | Scale from tanks/process units |
| Mixed wastes | | Domestic refuse, vegetation |
| Waste oils | | Lube oils, cut oils, transformer oils, recovered oils, engine oils |
| <i>Source:</i> [161, USAEPA 1995] | | |

Table 1.20: Waste generation declaration

| Waste types | Waste routes | 2007 | | 2009 | |
|-------------------------------------|--------------|--------------------|-----------------|--------------------|-----------------|
| | | Thousand tonnes/yr | Number of sites | Thousand tonnes/yr | Number of sites |
| Hazardous waste in country | Disposal | 294 | 103 | 405 | 105 |
| | Recovery | 306 | 98 | 372 | 103 |
| Hazardous waste outside the country | Disposal | 3 | 5 | 4 | 3 |
| | Recovery | 34 | 30 | 19 | 23 |
| Non-hazardous waste | Disposal | 372 | 60 | 262 | 59 |
| | Recovery | 538 | 61 | 500 | 64 |
| TOTAL | | 1547 | | 1562 | |

Source: E-PRTR and CONCAWE data 2007-2009

Oil retained in sludges or other types of waste represents a loss of product and, where possible, efforts are made to recover such oil. Waste disposal depends very much on its composition and on the local refinery situation. Because of the high operating costs of waste disposal, much priority has been given to waste minimisation schemes.

Waste generation trends show that oily sludge production is declining, mainly through housekeeping measures, whereas biological sludge generation has increased as a result of increased biotreatment of refinery effluent. Spent catalyst production is also increasing through the installation of new hydrocrackers, hydrotreatment facilities and catalytic cracker dust collectors. For all these waste categories, increased use is made of third party waste contractors for off-site treatment and disposal.

1.4.4 Soil and groundwater contamination

Most refineries have some areas that are contaminated by historical product losses. Current refinery practices are designed to prevent spillages and leaks to the ground. In the past, the awareness of the potential risks of these contaminated areas was low. The two main issues here are the prevention of new spills and the remediation or the remedial control of historic contamination. As mentioned within the scope, soil remediation is not included in the scope of this document.

The main sources of contamination of soil and groundwater by oil are typically those places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground. These are commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon-containing water. The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists.

1.4.5 Other environmental issues

Besides the environmental issues mentioned in the above sections, especially for refineries situated near residential areas, environmental nuisances have become an issue of discussion with both local authorities and with representatives of the local population in so-called neighbourhood councils. Topics such as noise, light, smoke emission (flaring) and odour which directly impact the residents receive much more emphasis in these neighbourhood councils than the above-mentioned 'major' emissions which tended to receive more attention historically.

Aggravation by light can be caused through flaring at night by refineries and petrochemical plants located near densely populated areas.

A potential environmental issue regarding heat discharged by cooling water to the sea or rivers may also be considered.

Occupational health is included in the operational safety procedures aimed at protecting workers from exposure to toxic materials and providing them with all necessary facilities which contribute to their well-being and their sense of security and safety. Instructions, information exchange and the training of personnel, the provision of personal protection equipment, as well as strict adherence to stringent operational procedures, have contributed to a steady decrease in accidents and health incidents. Typical refinery pollutants and products with a health risk include hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NO_x and SO_x, for which legally binding maximum acceptable concentrations values prevail.

The design of the refinery installations and the process control systems need to include provisions for a safe shutdown with minimum emissions from the unit involved. During unplanned operational upsets, these provisions should guarantee that feed supply is terminated followed by subsequent pre-programmed automated activation of pumps, relief systems, purging systems, flares and other equipment. Examples of such occurrences are utility failure, the breakdown of equipment, a fire or an explosion. Emergency situations leading to direct spills occurring in parts of the plant which are neither fully contained nor fully automated, such as pipeline and tank bottom rupture, have to be addressed with standing emergency procedures. Such procedures should aim at the minimisation and containment of the spills, followed by the rapid clean-up, in order to minimise the environmental impact.

2 APPLIED PROCESSES AND TECHNIQUES

This chapter describes the major activities and processes that may be found within the natural gas plant sector and the petroleum refining industry, including the materials and equipment used and the processes employed. This chapter is designed for those interested in gaining a general understanding of the processes and activities that can be found in these two industrial sectors, and for those interested in the interrelationship between the industrial process and the topics described in subsequent chapters of this document, which include emissions, consumption and best available techniques for the different processes. This chapter does not attempt to replicate published engineering information that is available for this industry in the general literature.

The major production unit operations and activities typically carried out in petroleum refineries are briefly described, in alphabetical order. For many of these production operations, a number of different techniques and/or unit operations are used in the industry. While the major techniques used for each process/activity are described, the intention is not to describe all the different processes currently in use. This chapter specifically describes the purpose and principles of the processes, feed and product streams, and a brief process description of commonly used production processes/activities and operability. This information, coupled with schematic drawings of the identified processes, provides a concise description of the relevant processes/activities.

The first section is dedicated to a general technical description of refineries; the subsequent other sections cover all the processes and activities within the scope of the BREF. The processes related to natural gas plants are included in one independent section (Section 2.17). These sections do not pretend to be of equal importance from the environmental impact point of view. Some sections have more relevance than others, but this approach allows for clearer presentation of the BAT assessment for the mineral oil and gas refinery sectors. No pollution abatement techniques are included in this chapter. However, some of the processes (e.g. hydrotreatments) have an environmental aspect. Environmental implications of production techniques can be found in Chapter 3. Discussions on good environmental practices (prevention techniques) for production techniques can be found in Chapter 4. As a consequence, no information about emissions is generally presented in Chapter 2. Information on, for instance, flares, sulphur recovery units, waste water systems and waste management is not included in this chapter because these activities are not considered production activities. They are security or environmental techniques that are applied in both sectors.

2.1 General overview of refinery processes

Crude oil and natural gas are mixtures of many different hydrocarbons and small amounts of impurities (see Annex 8.2.1). The composition of these raw materials can vary significantly depending on the source. Refineries are complex plants, where the combination and sequence of processes are usually very specific to the characteristics of the raw materials (crude oil and natural gas) and the products to be produced. In a refinery, portions of the outputs from some processes are fed back into the same process, fed to new processes, fed back to a previous process or blended with other outputs to form finished products. One example of this can be seen in Figure 2.1, which also shows that refineries are all different regarding their configuration, process integration, feedstock, feedstock flexibility, products, product mix, unit size and design and control systems. In addition, differences in owner strategy, market situation, location and age of the refinery, historic development, available infrastructure and environmental regulation are among other reasons for the wide variety in refinery concepts, designs and modes of operation. Given these differences, it is hardly surprising that the environmental performance can also vary from refinery to refinery.

The production of a large number of fuels is by far the most important function of refineries and will generally determine the overall configuration and operation. Nevertheless, some refineries also produce valuable non-fuel products, such as feedstocks for the chemical and petrochemical industries. Examples are mixed naphtha feed for a steam cracker, recovered propylene, butylene for polymer applications and aromatics manufacture covered under the Large Volume Organic Chemical Industry BREF [85, COM 2003]. Other speciality products from a refinery include bitumen, lubricating oils, waxes and high-grade coke for industrial use. Some refineries may even be dedicated to the production of these products.

The refining of crude oil into usable petroleum products can be separated into **two phases** and a number of **supporting operations**.

The first phase is the desalting of crude oil (Section 2.9) and the subsequent distillation into its various components or ‘fractions’ (Section 2.19). A further distillation of the lighter components and naphtha is carried out to recover methane and ethane for use as refinery fuel, LPG (propane and butane), gasoline-blending components and petrochemical feedstocks. This light product separation is done in every refinery.

The second phase is made up of three different types of ‘downstream’ process: i.e. breaking, combining, and reshaping fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. The goal of these processes is to convert some of the distillation fractions into marketable petroleum products (see Section 8.2) through a combination of downstream processes. These processes define the various refinery types, of which the simplest is the ‘hydroskimming’, which merely desulphurises (Section 2.13) and catalytically reforms (Section 2.6) selected cuts from the distillation unit. The amounts of the various products obtained are determined almost entirely by the crude composition. If the product mix no longer matches the market requirements, conversion units can be added to restore the balance.

Market demand has for many years obliged refineries to convert heavier fractions to lighter fractions with a higher commercial value. These refineries separate the atmospheric residue into vacuum gas oil and vacuum residue fractions by distillation under high suction (Section 2.19), and then feed one or both of these cuts to the appropriate conversion units. Thus, by the inclusion of conversion units, the product slate can be altered to suit market requirements, irrespective of the crude type. The number and the possible combinations of conversion units are large.

The simplest conversion unit is the thermal cracker (Section 2.22), by which the residue is subjected to such high temperatures that the large hydrocarbon molecules in the residue convert

into smaller ones. Thermal crackers can handle virtually any feed, but produce relatively small quantities of light products. An improved type of thermal cracker is the coker (Section 2.7), in which all of the residue is converted into distillates and a coke product. In order to increase the degree of conversion and to improve product quality, a number of different catalytic cracking processes have evolved, of which fluid catalytic cracking (Section 2.5) and hydrocracking (Section 2.13) are the most prominent. Recently, residue gasification processes (Section 2.14) have been introduced within refineries, which enable refineries to eliminate heavy residues completely and to convert them into clean syngas for captive use and to produce hydrogen, steam and electricity via combined cycle techniques.

Supporting operations are those not directly involved in the production of hydrocarbon fuels but that serve a supporting role. They may include energy generation, waste water treatment, sulphur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and the storage of products.

Table 2.1 summarises the main products obtained from the main refinery processes. As can be seen, many of the products are obtained from different units. This is one aspect of the technical complexity and the variety of modes of operation that can be found in a refinery.

An overview of the general scheme of a complex refinery is provided in Figure 2.1. This figure can be used as a synopsis of Chapters 2, 3 and 4 of this document. For each of the displayed units or processes, it provides, in particular (in red), the corresponding section number which is used over these three chapters, according to the general structure given in the Scope section.

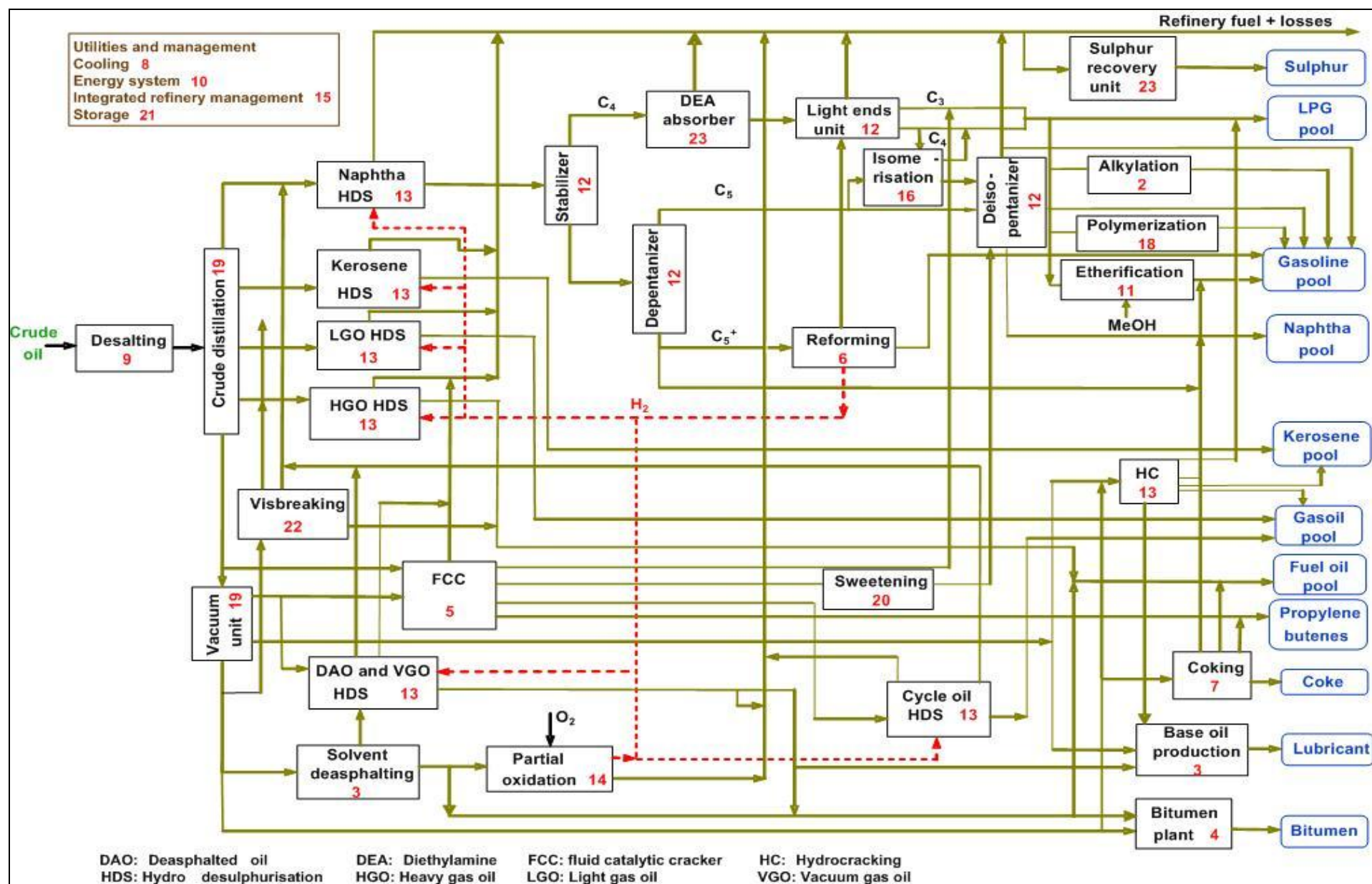


Figure 2.1: General scheme of a complex oil refinery

Table 2.1: Refinery units and their main products

| Products → refinery units | Section | LPG | Gasoline | Kero/naphtha | Heating oil/diesel | HFO | Base oil | Coke/bitumen | Special |
|--------------------------------|---------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------|------------------|------------------|--|
| Carbon number range | | C ₃ -C ₄ | C ₄ -C ₁₂ | C ₈ -C ₁₇ | C ₈ -C ₂₅ | >C ₈ | >C ₁₅ | >C ₃₀ | |
| Alkylation | 2 | | | | | | | | |
| Base oil production | 3 | | | | | | | | Waxes, White Oil, Extracts, Bright Stock |
| Bitumen production | 4 | | | | | | | | |
| Catalytic cracker | 5 | | | | | | | | |
| Residue cracking | 5 | | | | | | | | |
| Catalytic reforming | 6 | | | | | | | | H ₂ |
| Delayed coking | 7 | | | | | | | | |
| Flexicoker | 7 | | | | | | | | Low joule gas |
| Gasification | 10 | | | | | | | | Syngas |
| Etherification | 11 | | | | | | | | MTBE |
| Gas separation processes | 12 | | | | | | | | Refinery fuel gas |
| Hydrogen plant | 14 | | | | | | | | H ₂ |
| Residue hydroconversion | 14 | | | | | | | | H ₂ |
| Hydrocracker | 15 | | | | | | | | |
| Hydrodesulphurisation | 15 | | | | | | | | |
| Isomerisation | 17 | | | | | | | | |
| Crude atmospheric distillation | 19 | | | | | | | | |
| Vacuum distillation | 19 | | | | | | | | |
| Thermal cracking/Visbreaking | 22 | | | | | | | | |
| Sulphur recovery unit | 23 | | | | | | | | S |

2.2 Alkylation

Purpose and principle

The purpose of alkylation is to yield high-quality motor fuel after blending. The term alkylation is used for the reaction of olefins with isobutane, to form higher molecular-weight isoparaffins with a high octane number. The process involves low-temperature reaction conditions conducted in the presence of strong acids.

Feed and product stream

Low molecular weight olefins (C_3 - C_5) and isobutane are used as alkylation unit feedstocks. The major sources of low olefins are catalytic crackers and cokers. Isobutane is produced by hydrocrackers, catalytic crackers, catalytic reformers, crude distillation and natural gas processing. In some cases, n-butane is isomerised (see Section 2.16) to produce additional isobutane. The product is alkylate (a high-octane gasoline component) with some propane and butane liquids. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range. Dissolved polymerisation products are removed from the acid as thick dark oil.

Process description

Two processes have dominated historically, with hydrofluoric acid (HF) or sulphuric acid (H_2SO_4) used as a catalyst. When the concentration of acid becomes low, some of the acid must be removed and replaced with fresh acid. Safety incidents and accidents in HF units over the years have led to changes:

- Sulphuric acid has dominated in new investments since 1980.
- Additives are now available to reduce the HF volatility and several mitigation systems have been developed to improve safety.
- Solid-acid catalyst alternatives have improved in later years but industrial sites have not yet reported successful start-up or operational results. The Baku Heydar Aliyev Refinery (Azerbaijan) [75, OandG Journal 2011] selected a solid-acid alkylation unit for their basic design. A solid-acid catalyst alkylation unit is under construction at the Shandong Petrochemical Group Company (China) for a start-up in 2014. Several available commercial processes are described in Section 6.2.1.3.
- Ionic liquid technology has been the subject of new patents and developments. A 65 000 tonnes per year plant in China has been retrofitted and has reported successful results (see Chapter 6). There are also techniques to facilitate the retrofitting of a HF plant into a H_2SO_4 unit.

Safety and environmental concerns are extremely important when choosing an alkylation technology. HF is specifically hazardous due to possible skin penetration and destruction at tissue levels (and pulmonary oedema). In Section 4.2.3, the trade-off between process alternatives is described.

In the hydrofluoric acid process, the acid slipstream is redistilled. The concentrated hydrofluoric acid is recycled and its net consumption is relatively low. In this process (Figure 2.2), the feed enters the reactor and is mixed with the recycled isobutane and HF from the settler. Both the olefin and isobutane feeds are dehydrated first (not shown in Figure 2.2), as this is essential to minimise the potential corrosion. The reactor, operating at 25 – 45 °C and 7 – 10 barg, is cooled to remove the heat generated by the reaction. In the settler, alkylate and excess isobutane are separated from the HF. The HF is recycled to the reactor. A slipstream is regenerated by distillation. The organic phase from the settler, consisting of the alkylate and unreacted isobutene, flows to the isostripper. There, the isobutane and some other light components are stripped from the alkylate. This is routed as product to storage after treating it with potassium hydroxide (KOH). The decomposition of any organic fluoride formed is promoted by the high tube wall temperatures. Saturated butanes are normally distilled outside the alkylation unit to produce a concentrated stream of isobutane, which is fed to the alkylation unit with the olefin feed. The isostripper overhead, essentially isobutane, is returned to the

reactor. A small overhead slipstream is sent to a depropaniser, where propane is removed. The bottoms of the depropaniser (isobutane) are routed to the isobutane circulation stream, while the depropaniser overhead stream (propane) passes through a HF stripper to remove traces of HF and is sent to storage after final KOH treatment. Normal butanes which come in with the unit feed streams are drawn off as a side-stream from the isostripper, treated with KOH and sent to storage.

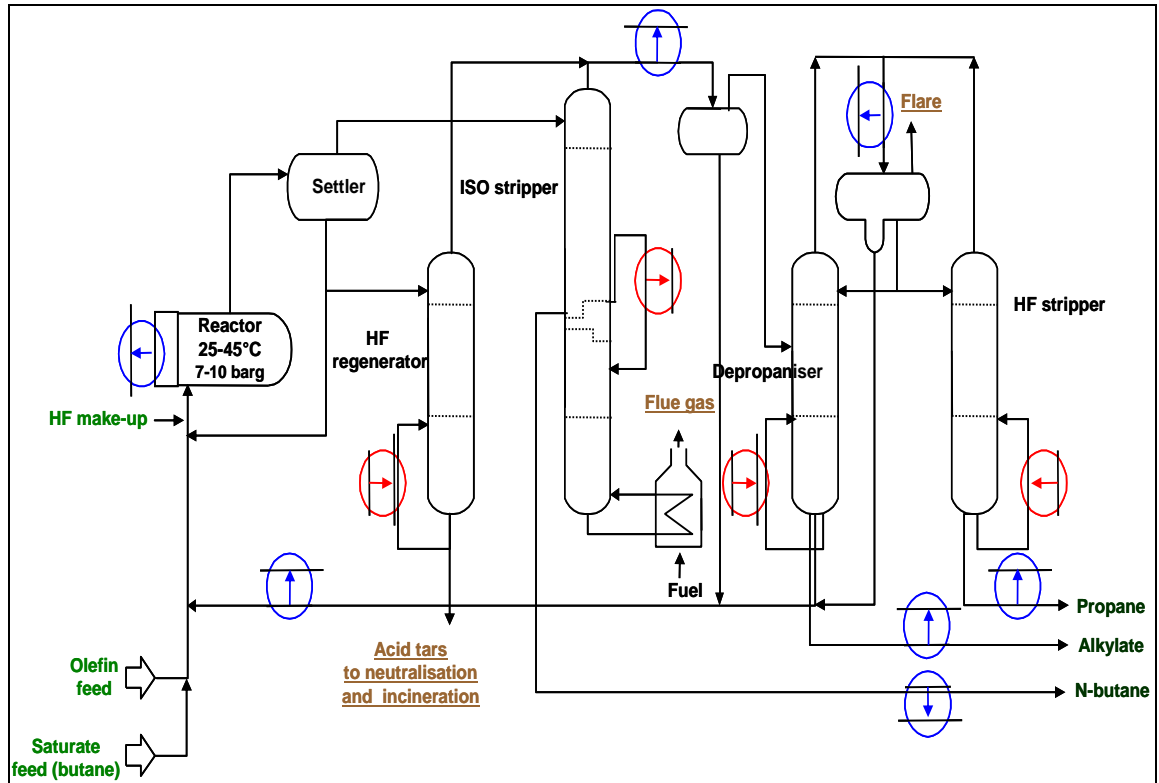


Figure 2.2: Simplified process flow scheme for a HF alkylation unit

In the sulphuric acid process (see Figure 2.3), the aim is to produce high-octane branched chain hydrocarbons for the gasoline pool. The process combines olefin and butylene feeds in the presence of strong sulphuric acid. The feed contacts the recycle stream of H_2SO_4 in the reactor. The reactor circulation stream enhances a large interface area at low temperatures (4 – 15 °C). Reaction products are first separated in a flash drum and then through a debutaniser. On-site acid regeneration is also possible (i.e. WSA technique).

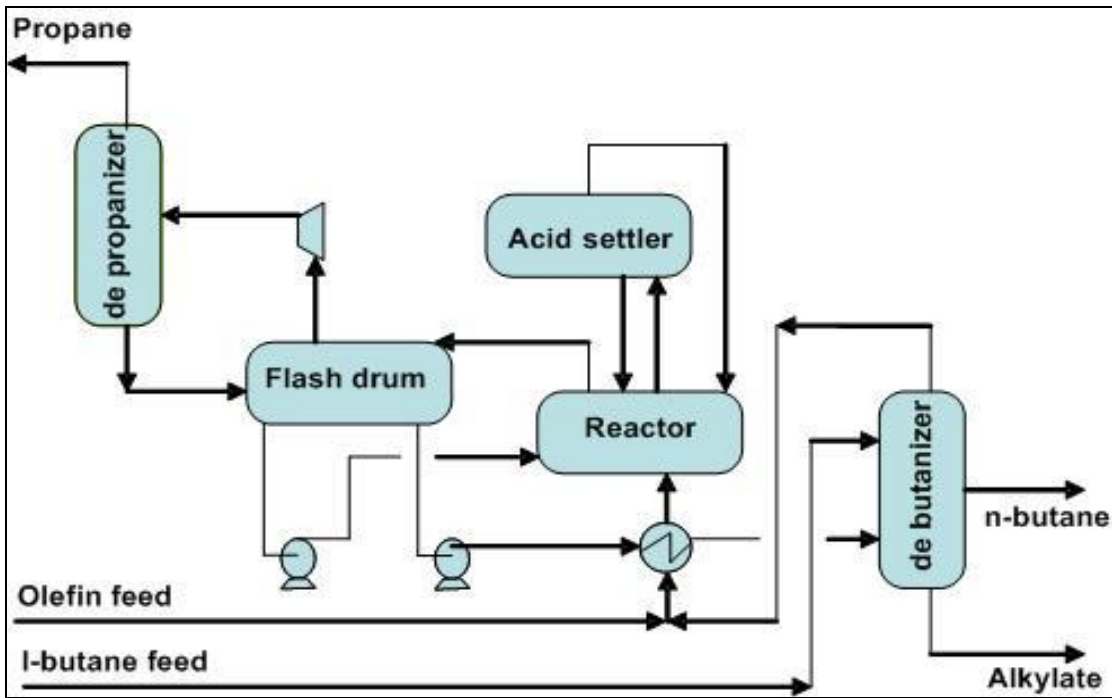


Figure 2.3: Simplified process flow scheme for sulphuric acid alkylation

The AlkyClean solid-acid process is covered as an emerging technique in Chapter 6.

2.3 Base oil production

Although only 20 % of EU refineries produce base oil, some actually specialise in it.

Figure 1.7 and the associated table (in Chapter 1) identify the refineries specialised in the production of lubricant and bitumen. More extensive information about the processes can be found in the general literature (e.g. [231, Sequeira 1998]).

Purpose and principle

Lubricants are a blend of different grades of base oils and special additives. To produce a suitable lubricant, certain properties of the base oil are very important: viscosity, viscosity index (VI: a high VI means that the viscosity changes very little as the temperature changes, and vice versa), high resistance to oxidation, low pour point and good dope susceptibility or compatibility.

Base oil is a speciality product and consequently not all crudes are suitable. Heavy crudes are frequently used as feedstock for conventional base oil complexes. New processes based on catalytic hydrogenation reactions enable a wider variety of feeds.

Feed and product stream

The feedstocks of a conventional base oil complex are waxy distillate side-streams from vacuum distillation units (Section 2.19) and the extracts from deasphalting units. Atmospheric residue feedstock to the vacuum distillation unit consists of various types of hydrocarbon compounds with different suitability for base oils, e.g.:

- **Aliphatic or paraffinic:** Normal (n-)paraffins and iso (i-)paraffins form this group. The n-paraffins have high VI and melting points, and at ambient conditions form crystals, which must be removed to reduce the pour point of lubricating oils. I-paraffins have lower melting points, very high VI but lower viscosity.
- **Naphthenic:** The naphthenic rings lend high viscosity, a low melting point and a good VI (less than paraffins) to lubricant oils.
- **Aromatic:** The aromatic rings lend high viscosity and a low melting point to compounds but a low VI to the oils. For this reason, they are considered the least satisfactory type of compounds for lubricants. The ratio in which the three groups are present varies from crude to crude.

New industrial facilities can also use natural gas as a feedstock (gas-to-liquid processes).

The American Petroleum Institute (API) has developed a base oil classification system which categorises base oils into five major groups, classified on the basis of the following three criteria:

- The percentage of saturates (the higher the number of saturates, the better the resistance to breakdown or loss of viscosity).
- The sulphur content (the lower the sulphur content, the better the purity: thus the product is less corrosive and there is less potential for oxidation).
- Viscosity index (the VI is an indication of the rate of change of viscosity against temperature, and the higher the VI, the better). The viscosity is the oil resistance to flow and shear. It is the single most critical physical property of the oil, as it affects both the wear rate and the fuel efficiency.

The five groups defined by the API are:

- Group I: Contains less than 90 % saturates and/or greater than 0.03 % sulphur and has a VI between 80 and 120. Demand is around 65 %, with a decreasing trend.

- Group II: Contains more than 90 % saturates and less than or equal to 0.03 % sulphur and has a VI from 80 to 120. The demand is around 25 % and tends to go up.
- Group III (known as unconventional base oils - UCBO): Contains more than 90 % saturates and less than or equal to 0.03 % sulphur and has a VI of more than 120. Groups III and II oils are made by the same process, but for group III, the VI is increased by higher temperature in the hydrocracker or by appropriate crude selection as a feedstock. Group III advantages over group I and II base oils are that it is more fuel-efficient, has longer drain intervals, is environmentally friendly and is engine-protective. Demand is around 10 % with a growing trend.
- Group IV: Synthetic base oils.
- Group V: All other base oils.

Process description

The marketplace is constantly seeking new lubricants, which in turn require an even higher base oil purity, higher viscosity index, lower volatility, and longer life.

There are many possible routes for improving base oil quality and extending the product variety among the main four following process families including:

Separation by solvent-based processes

Solvent-based processes aim to remove the different impurities from the feedstock by extracting the undesired components.

Conversion by hydrogenation-based processes [137, Szeitl et al.2008]

The hydrogen conversion (HC) and catalytic dewaxing (CDW) technology converts undesired components directly into end products. The base oils are hydrofinished at higher pressure (>100 bars) than the around 30 bars pressure applied in conventional manufacturing. This technology has significantly lower operational costs but a substantial initial investment. It can process a wider range of feedstock, but has a much narrower product range compared to solvent-based production (e.g. Bright Stock, the upper end of group I base oils specifications). It produces non-carcinogenic naphthenic base oils and removes impurities such as nitrogen, sulphur or oxygenated compounds.

Converting to hydrogen-based processes: Hybrid [252, Ullmann's 2012]

Lower hydrogen usage may lead to lower operational costs. There are many combinations for revamping or debottlenecking existing units. Operators can run the alternative routes in parallel plants or can have upstream units based on hydrogenation together with downstream solvents-based ones. The opposite combination is generally not viable because the CDW catalyst can only receive low nitrogen and sulphur content (high-pressure hydrotreated) feedstock.

Gas to Liquid (GTL)

Liquefaction of natural gas and the chemical reaction route were developed on the basis of the Fischer–Tropsch process. This process creates high-quality liquid products and paraffin wax. High VI oils can then be obtained from natural gas by partial oxidation, polymerisation and isomerisation. The GTL process provides products with high biodegradability and the absence of sulphur, nitrogen, and aromatics compounds. At a global level, GTL is still a new industry with a limited number of commercially operative plants. A number of GTL plants are in operation in South Africa (Sasol: 8 Mt/yr, PetroSA: 1 Mt/yr), in Qatar (Sasol-Qatar Petroleum Oryx: 1.7 Mt/yr), and Malaysia (Shell: 0.6 Mt/yr). Global GTL capacity is expected to increase to more than 25 Mt/yr by 2015. More than 50 % of the global GTL capacity will be in Qatar (new construction units for about 20 Mt/yr additional capacity) [273, O&Gas Journal 2010].

The appropriate options to produce high-quality base oils depend on the refinery's crude oil processing flexibility, the existing units, and the capital-cost tolerance. The new, higher quality base oil refining processes have the lowest cost of production. These new base oil plants are less crude-sensitive, offer synergy with fuels strategy, provide high quality and more valuable base oils together with better yield. Their drawback is the lack of heavy cut base stocks, therefore

there is a need to keep solvent technologies as well. Many European base oil plants are more than 30 years old, and most of these use solvent-based processes.

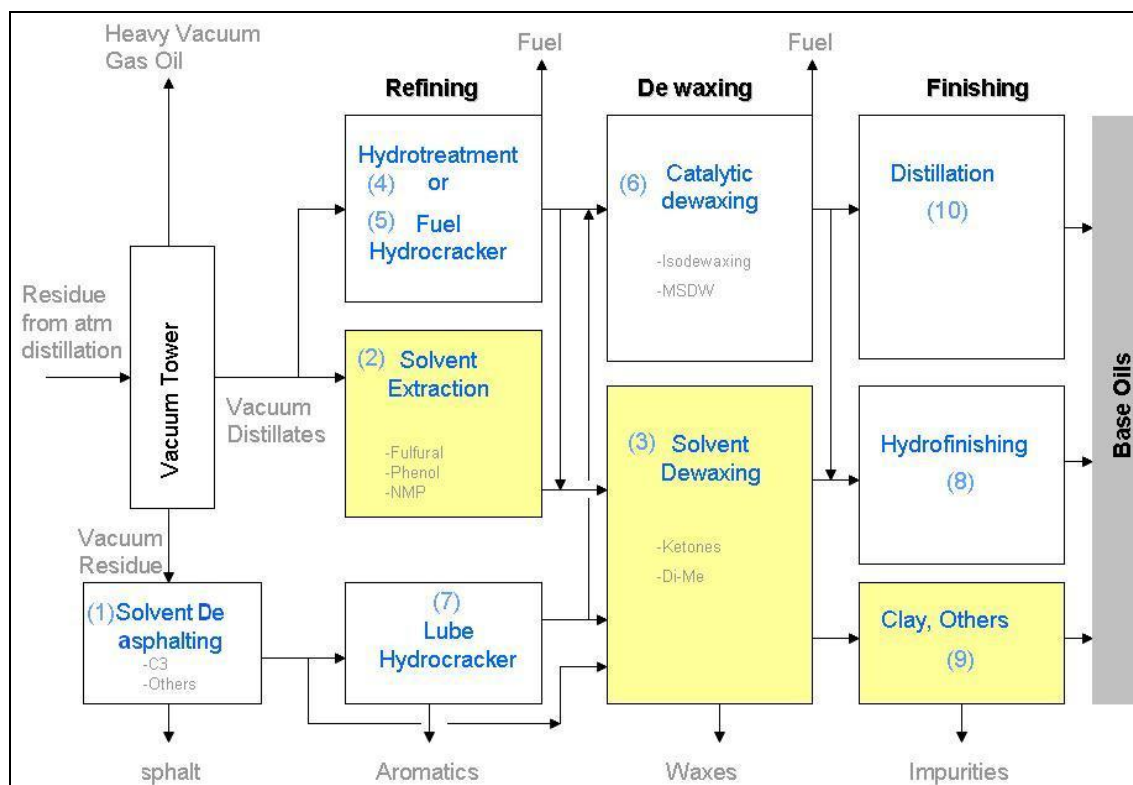


Figure 2.4: Block scheme of a lubricating oil manufacturing plant with a combination of process options units

Each of the process steps shown in Figure 2.4 are described below:

(1) Solvent deasphalting

- Target: Extracting high-boiling lighter paraffinic and naphthenic hydrocarbons (asphaltenes and resins) from the vacuum distillation unit residue.
- Operations: Propane or propane-butane mixtures are usually used as solvents at specific operating conditions (37 – 40 bar and 40 – 70 °C). A typical extraction process consists of an extractor and recovery sections, flash evaporation and stripping. More recently, solvent deasphalting has been adapted for the preparation of catalytic cracking, hydrocracking, hydrosulphuriser feeds and hard bitumen (deep deasphalting). For these purposes, heavier-than-propane solvents (butane to hexane mixture) are used, together with higher operating temperatures.
- Features: Propane from the low-pressure or stripping section can be recovered within the process by distillation and stripping (with a corresponding energy consumption). Remaining traces of solvent are very often used as a fuel gas.

(2) Solvent-based aromatic extraction [253, CONCAWE 2012]

- Target: Removing aromatics from base oil feedstocks, improving viscosity, oxidation resistance, colour and gum formation.
- Operations: Different solvents can be used (furfural, N-methyl-2-pyrrolidone (NMP), phenol, cresol or liquid sulphur dioxide). These processes are typical extraction processes, consisting of an extractor and recovery sections, flash evaporation and stripping to separate the solvent from the oil-rich raffinate and aromatic-rich extract stream. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor. Solvents are recovered from the oil stream through distillation and

steam stripping in a fractionator. The raffinate stream is run down to intermediate storage. The extract, after solvent recovery, is likely to contain high concentrations of sulphur, aromatics, naphthenes and other hydrocarbons, and is often fed to the hydrocracker or catalytic cracker unit. Depending on the different physico-chemical properties (e.g. boiling and melting points) of the applied solvents, the physical design and construction of the aromatic extraction units are different (boiling point for NMP: 202 °C; for furfural: 162 °C. Melting point for NMP: -23.6 °C; for furfural: -37 °C).

- Features: Process designs need to consider many factors. When the solvent volume in the process can be reduced, less energy consumption for evaporation is needed. NMP is more corrosive than clean furfural. Furfural tends to degrade and coke within the process, raising solid waste. The waste water from aromatic extraction can be treated separately before leaving the unit. Operating this pretreatment, the solvents are recovered and kept in the system. In recent years, several furfural extraction plants have been converted into NMP plants, and even phenol plants have a lower priority. NMP is a less toxic solvent and can be used in a low solvent-to-oil ratio with high selectivity. This generates significant energy savings. NMP in new plants generally results in physically smaller units and thus lower capital expenditure.

(3) Solvent dewaxing [253, CONCAWE 2012]

- Target: Ensuring that the oil has the proper viscosity at lower ambient temperatures. Paraffins are removed.
- Operations: Feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallised, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK), toluene or chlorinated hydrocarbons, such as a mixture of 1,2-dichloroethane and dichloromethane (Di-Me). The solvents are chosen according to the focus of the dewaxing process:
 - When aiming to remove paraffinic compounds from the feedstock in order to achieve high yields of base oil, a mixture of MEK/toluene or MEK/MIBK might be chosen.
 - When aiming to produce specific oil and wax qualities with special product requirements, the preferred solvent is a Di-Me mixture. The chlorinated solvents used in the dewaxing/de-oiling process usually are 1,2-dichloroethane (DCE) and dichloromethane (DCM). The mixture (Di-Me) varies from 80/20 to 20/80, according to the feedstock to be treated.
 - When the units are designed to de-oil slack wax of various qualities, a single solvent, 1,2-Dichlorethane, is generally used.
- Features: Solvent is recovered from the oil and crystallised wax through heating, two-stage flashing, followed by steam stripping. The wax is removed from the filters, melted and subsequently fed to a solvent recovery unit to separate the solvent from the wax.

(4) High-pressure hydrogenation unit

- Target: Stabilising the most reactive components in the base oil, improving the colour, and increasing the useful life of the base oil. This process removes some of the nitrogen- and sulphur-containing molecules but is not severe enough to remove a significant amount of aromatic molecules.
- Features: Adding hydrogen to the base oil at elevated temperatures in the presence of catalyst. Hydrotreating represents only a small improvement in base oil technology.

(5) Hydrocracker

- Target: The molecules of the feed are reshaped and often cracked into smaller ones. A great majority of the sulphur, nitrogen, and aromatics are removed. Molecular reshaping of the remaining saturated species occurs as naphthenic rings are opened and paraffin isomers are redistributed. Produces fuel and base oil; higher purity than solvent-based process; lower aromatic content.
- Operations: Add hydrogen to the base oil feed at higher temperatures and pressures than simple hydrotreating. The process is driven by thermodynamics, with reaction rates facilitated by catalysts.

- Features: Since 1995, more than 50 % of new plants use this technology. The return on investment is fairly quick, since the fuels are sold almost immediately.

(6) Catalytic dewaxing

- Target: As an alternative to solvent dewaxing, especially for conventional neutral oils, catalytic dewaxing removed n-paraffins and waxy side chains from other molecules by cracking them into smaller molecules. This process lowered the pour point of the base oil so that it flowed at low temperatures, like solvent dewaxed oils. Since 1995, more than half of all new base oil manufacturing plants have been built or are planned using hydrocracking technology. A number of different catalytic dewaxing processes have been developed and based on appropriate catalysts (generally zeolites) to perform three main classes of chemical transformations, aiming at increasing the VI and good low-temperature characteristics:
 - Ring conversion: opening the heterocycle into a more aliphatic structure by the ejection of heteroatoms such as nitrogen or sulphur embedded in structurally hindered rings, ring de-alkylation of multiring hydrocarbons.
 - Paraffins conversion: this step can be performed by a family of processes, and involves the boiling point conversion of the paraffin components of waxy feeds by selective hydrocracking or by selective hydro-isomerisation.
 - Saturation: to ensure the oxidative stability of base stocks a sufficient extent of ring hydrogenation (saturation) is needed.
- Operations: With suitable catalysts, it enables the use of cheaper feeds and produces high value C5 byproducts. Different reaction arrangements are available and subsequent process combinations are possible.
- Features: About 90 refineries in the world use this process.

(7) Lube unit

- Target: Lube unit converts the vacuum gas oil to low pour point, high VI stable lubricant base oils, mainly by cracking low-VI components and saturating aromatics.
- Operations: The process takes place at high pressure and temperature with hydrogen and a catalyst. The feed is processed over fixed bed reactors. The products are then fractionated in a distillation section, where columns are reboiled with hot oil.

(8) Hydrofinishing

- Target: In this unit, the colour and colour stability are improved and the organic acid components are removed. Sulphur content is also reduced.
- Operations: The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).
- Features: In stand-alone base oil refineries, the small amounts of H₂S generated due to hydrotreatment are normally incinerated or burnt as a component of fuel if a Claus unit is generally not available. The need for hydrofinishing depends on the crude oil processed and to a certain extent on the patent owner and the design of the preceding units.

(9) Clay treatment

Instead of hydrotreatment, sulphuric acid and clay treatments may typically be used in old plants. Additional finishing with absorbents (bleaching clays, bauxite) may be used with certain oils specifications (e.g. for transformers, refrigerators, or turbines. The filtration process represents additional complexity and the residues need to be appropriately disposed of).

(10) Distillation

Depending on the upstream process selected, some base oil complexes may need a final separation of products with a fractionation train. This is normally done with several distillation columns, potentially under vacuum, that may also withdraw some remaining impurities.

Reference literature

[76, *Hydrocarbon processing* 2011], [137, Szeitl et al.2008], [251, *Credit Suisse* 2012], [252, *Ullmann's* 2012], [273, *O&Gas Journal* 2010].

2.4 Bitumen production

Bitumen is a residue derived from certain crude oils (e.g. Middle East, Mexico or South America) after vacuum distillation has removed waxy distillates. Bitumen is normally mixed with other components (e.g. gravel) to produce asphalt that is used in road paving, roof coating and pipe sealing or coating. Bitumen production only appears in some refineries (45 % of the EU refineries). There are also some refineries that specialise in producing these components. Figure 1.7 (in Chapter 1) and the associated table identifies the bitumen-specialised refineries.

Purpose and principle

The desired properties of bitumen may be achieved either by adjusting distillation conditions or by ‘blowing’. In the latter process, air is blown into hot bitumen causing dehydrogenation and polymerisation reactions and creating a harder product with higher viscosity, higher softening point and a reduced penetration. (The penetration, often used as the main criterion, refers to the depth of penetration by a standard needle in a bitumen sample at standard conditions). The properties of the blown bitumen are determined by the residence time in the oxidation vessel, the air rate and the liquid temperature. If any of these parameters are increased, the penetration is reduced and the softening temperature is raised.

Feed and product streams

In most applications, the hydrocarbon feed stream to a bitumen blowing unit (BBU) is the bottom residue stream from a vacuum unit (Section 2.19) and in some instances the residue (extract) from a deasphalting unit (Section 2.3).

Normally, a number of different grades of bitumen are produced in campaigns and these are further modified by blending with other high-boiling components such as vacuum residue, heavy gas oil or synthetic polymers. In this way, a single blowing unit is able to cater for a wide range of bitumen grades for various applications.

Polymer additives Styrene Butadiene Styrene (SBS), Ethylene Vinyl Acetate (EVA), Natural rubber, etc. are used for heavy duty service bitumen production. They do not change the chemical structure of the bitumen but change its mechanical properties. The polymers modify the bitumen’s properties such as the softening or brittleness point, and aim at improving longevity.

Process description

The BBU will either operate on a continuous basis or in batch mode depending on the quality of the vacuum residue feedstock and the required bitumen product specification. Continuous processes are the most common in refineries. A simplified process flow diagram of the BBU is shown in Figure 2.5, which represents a typical, continuously operated BBU receiving its hot feed directly from the vacuum distillation unit. Where the bitumen feed is received from storage, an additional fired heater may be required to preheat the feed to a temperature of about 200 – 250 °C, but it can be up to 550 °C. With a batch-operated BBU, a feed buffer vessel is usually included to store the hot feed stream from the vacuum unit.

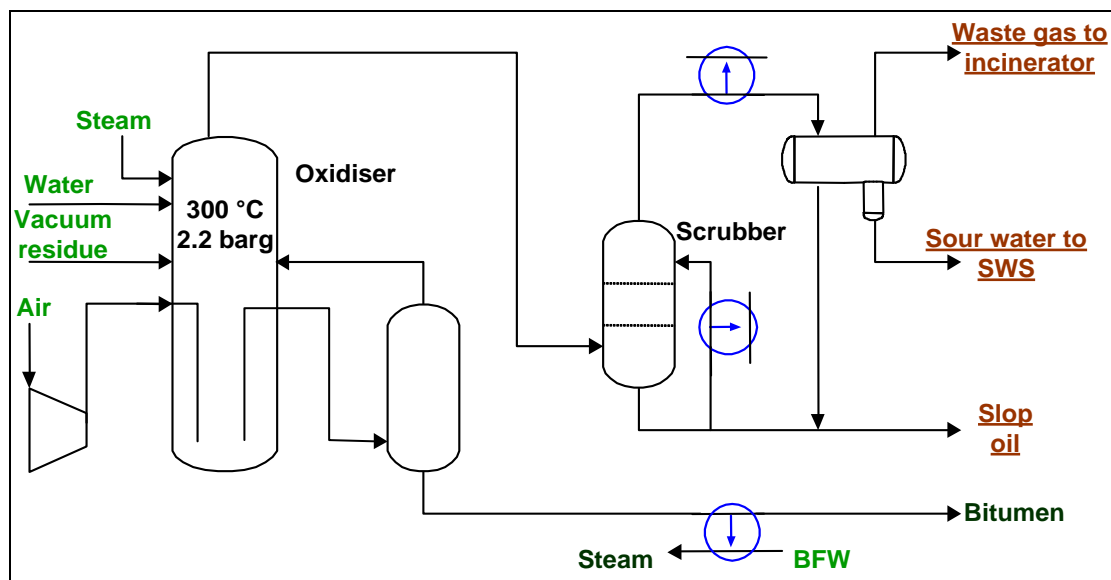


Figure 2.5: Simplified process flow scheme of a bitumen blowing unit

The residue feed stream is pumped into the top of the oxidation vessel. The operating pressure in the top of the oxidation vessel is normally around 1 barg and in the bottom around 2 barg, depending on the height of the vessel. As air is sparged into the base of the vessel, oxidation of the residue takes place, resulting in heat. The temperature in the oxidation vessel, which determines to a certain extent the bitumen grade, is normally controlled between 260 °C and 300 °C. Different options are applied for adjusting the temperature, which include the addition of colder feed to the oxidation vessel, the recirculation of cooled bitumen product from the bitumen run down cooler, and in older units direct water quenching. The blown bitumen is removed from the bottom of the oxidation vessel and cooled by rising steam, before being sent to storage.

The air rate is normally well in excess of stoichiometric requirements and so a considerable quantity of oxygen is present in the upper vapour space of the oxidation vessel. To avoid an explosion in the vapour space, in most units, steam is injected at a rate necessary to keep the oxygen concentration below the lower flammable limit (5 – 6 % v/v). In some units, a small amount of water is also injected into the vapour outlet of the oxidation vessel to reduce the vapour temperature. This is sometimes considered necessary to prevent afterburning in the overhead system which could otherwise lead to severe coke formation.

The overhead vapours are first passed through a vent gas scrubber to remove oil and other oxidation products. In most cases, gas oil is used as once-through scrubbing liquid. The vent gas from the scrubber is subsequently cooled to condense light hydrocarbons and sour water, sometimes in a water spray contact condenser or scrubber. The remaining gas, consisting mainly of light hydrocarbons, N₂, O₂, CO₂ and SO₂, is incinerated at high temperatures (~800 °C) to ensure complete destruction of minor components such as H₂S, complex aldehydes and organic acids and phenolic compounds, which have a highly unpleasant odour.

The majority of the BBUs produce the higher grades of bitumen (roof and pipe coatings) and normally operate continuously throughout the year. The BBUs which are used to produce road bitumens operate only when the demand for road asphalt is high.

2.5 Catalytic cracking

Purpose and principle

Catalytic cracking is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons. In 2008, 56 fluid catalytic cracking (FCC) units were installed in the EU-27. It uses heat and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Unlike the hydrocracker process, no hydrogen is used and, consequently, limited desulphurisation takes place. Compared to other heavy oil catalytic conversion processes, the fluid catalytic cracking (FCC) process is superior in being able to handle larger quantities of metals, sulphur and asphaltenes. One drawback is the limited flexibility in changing the product yields, even if recent developments in catalysts allow, depending on the catalyst selection, an increase of the LPG yield or a further reduction of the bottom products.

Feed and product streams

Fluid catalytic cracking units can be designed to process heavy vacuum gas oils (HVGO) from the vacuum distillation unit, or bottom streams, also called 'long resid' (LR) from the atmospheric distillation unit. Most often, units designed for HVGO also treat some LR, and vice versa. These two unit types will be referred to as the FCC unit and the RCC unit respectively.

Other process streams may be blended into the catalytic cracker feed such as heavy gas oil from the atmospheric distillation unit, coker or visbreaker gas oil, deasphalted oil and extracts from base oil units and sometimes a small quantity of atmospheric residue. These streams may be hydrotreated to adjust the desired product's yields and properties.

Compared to other conversion processes, the catalytic cracker process is characterised by a relatively high yield of good quality gasoline and relatively high quantities of C₃ and C₄. Both products are highly olefinic and therefore are ideal feed streams for the alkylation, etherification and petrochemical industries. One drawback of this process is the very low quality of the mid-distillate products in terms of sulphur, olefins, aromatics and cetane index. The majority of the products need further treatment prior to storage.

Process description

A number of different catalytic cracking designs are currently in use worldwide, including fixed bed reactors, moving bed reactors, fluidised bed reactors and once-through units. The fluidised and moving bed reactors are by far the most prevalent in world refineries.

Fluid catalytic cracking (FCC) units are by far the most common catalytic cracking units. The FCC unit consists of three distinct sections, the reactor-regenerator section including the air blower and the waste heat boiler, the main fractionator section including the wet gas compressor and the unsaturated gas plant section. A simplified flow scheme is shown in Figure 2.6.

In the FCC process, oil and oil vapour preheated to 250 – 425 °C come into contact with hot catalyst at about 680 – 730 °C in the riser reactor. To enhance vaporisation and subsequent cracking, the feed is atomised with steam. The cracking process takes place at temperatures between 500 °C and 540 °C and a pressure of 1.5 – 2.0 barg. Most catalysts used in catalytic cracking contain zeolites (for more details on zeolites see Annex 8.4) with metals and rare-earth elements supported by different types of aluminas and clays. The catalyst is in a fine, granular form which mixes intimately with the vaporised feed. The fluidised catalyst and the reacted hydrocarbon vapour are separated mechanically in a (two-stage) cyclone system and any hydrocarbon remaining on the catalyst is removed by steam stripping. The amount of catalyst lost as fines in the reactor and regenerator cyclones is balanced by the addition of fresh catalyst.

The catalytic cracking processes produce coke, which collects on the catalyst surface and diminishes its catalytic properties. The catalyst therefore needs to be regenerated continuously essentially by burning the coke off the catalyst at high temperatures. The method and frequency with which catalysts are regenerated are a major factor in the design of catalytic cracking units.

The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration, done by burning off the coke deposits with air. However, in time, the catalyst deactivates gradually and irreversibly due to high-temperature exposure and metal poisoning (mainly vanadium). The hot regenerated catalyst flows back to the base of the reactor riser, where it is cooled by vaporisation of the feed and by the heat absorption required for cracking reactions.

The cracked hydrocarbon vapours are then fed to a fractionation tower where the various desired fractions are separated and collected. The streams are steam stripped to remove volatile hydrocarbons prior to cooling and sending to storage. Slurry oil is taken from the bottom of the column and is cooled by heat exchange with the reactor feed stream and by steam generation, and is then returned to the column. The recycled slurry oil is used as wash oil and as a quench for the hot reactor overhead vapours to prevent aftercracking. The rest of the slurry oil is filtered or decanted to remove catalyst fines, cooled and sent to storage. The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate it into three phases: gas, liquid and sour water streams. The liquid and gas streams are both fed to the gas plant (Section 2.12) for further separation and the sour water stream is sent to the sour water stripper for purification (Section 2.25).

Various types of equipment are usually used for recovering energy from this process. The hot flue-gases from the regenerator are cooled by means of steam generation in a waste heat boiler or, in case of partial CO combustion, in a CO boiler. Prior to steam generation, electricity can also be produced by expansion of the flue-gases in a turbo-expander. And, in particular for units processing large quantities of residue, additional heat removal from the regenerator can be achieved with catalyst coolers for steam generation.

Full combustion mode

Full combustion mode is typically applied to vacuum distillate feedstocks. Low Conradson carbon feeds are typically processed in full combustion FCCs.

In the full combustion mode, the following precautions should be taken in order to reduce the emission of pollutants:

- The amount of CO generated can be limited to a range from 35 mg/Nm³ to 250 mg/Nm³, with an excess of oxygen greater than 2 %, (continuous operations as a daily average). A CO oxidation promoter can be added to the regenerator to catalyse the oxidation of CO. However, this promoter also catalyses the oxidation of the fuel nitrogen in the coke, increasing the NO_x levels (especially NO). A platinum catalyst may promote the generation of N₂O. Consequently, the amount of CO promoter varies the relationship between the NO_x emissions and CO emissions. However, values of 300 – 700 mg/Nm³ of NO_x (3 % O₂) can be achieved.
- For residual feedstock cracking using antimony addition, NO_x emissions can rise to 1 000 mg/Nm³ (3 % O₂), if no other reduction technique is used.
- Minimisation of the use of aeration and purge steam can decrease particulate emissions significantly. Aeration/steam rates are based on achieving a stable catalyst circulation in the catalyst lines between the reactor and the regenerator.
- Stripping of the catalyst before reaction or before regeneration reduces the HC content in the coke to be burnt.
- Temperature adjustment in the riser by injection of a recycle stream above the zone of the fresh feed injection.
- Modification of the design and operation of the regenerator, especially to avoid high temperature spots that tend to increase the NO_x formation.

Considering dust emissions, the basic design of a FCC includes two-stage cyclones in the regenerator vessel, which prevent the bulk of the fine catalyst used from escaping from the system. However, smaller catalyst particles, mostly created by attrition in the circulating

system, are not easily retained by the two-stage cyclone system. Consequently, in many cases, other abatement techniques are included to complement the process abatement techniques discussed here.

A reduction of the regeneration temperatures under the usual conditions (700 – 750 °C) would not have a significant impact on the NO_x emissions but it will increase the CO concentration in the flue-gas and coke formation. A change in the design or operation of the regeneration may increase the CO concentration.

When excess O₂ is reduced to around 0.5 %, NO_x production is dramatically reduced. This is due to the increase in CO from less available O₂, which can help reduce NO_x back to N₂. However, many FCC/RCC units cannot operate at these low O₂ levels and still maintain regenerator temperatures within safe operating limits, and low O₂ levels will increase CO emissions. Finally, SO_x production is typically increased at low O₂ when SO_x additives are being used, since there will not be enough O₂ for the SO₂ to oxidise to SO₃ and be captured by the additive.

Partial combustion mode

In general, feed with a Conradson carbon figure up to 2 – 3 % may be treated in a ‘standard’ FCC without a CO boiler as well as partial-combustion FCC. A Conradson figure from 2 – 5 % would require a CO boiler and from 5 – 10 % a catalytic cooler would be needed. It should be noted that the above figures are only indicative and also depend on the severity of the cracking.

In the partial combustion mode, considerable CO is present in the flue-gas and it is consumed downstream of the regenerator in a CO boiler, both to recover the energy produced in a CO boiler and to meet environmental requirements. This system can be seen as two-stage regeneration in comparison with the full combustion mode, where a single regeneration step is present.

The use of a partial combustion mode together with a CO boiler (COB) generates, in general, less CO and NO_x emissions compared with full combustion. The use of a COB or with a high-temperature regeneration technology can significantly reduce CO emissions. CO achieved emissions are from less than 50 – 400 mg/Nm³ and typically below 100 mg/Nm³ (3 % O₂ daily average). In the COB, refinery fuel gas addition is required to incinerate CO (~900 °C). The advantage of partial combustion coupled with a COB is also to achieve lower NO_x emissions (100 – 500 mg/Nm³ at 3 % O₂, daily average, standard conditions), ammonia and hydrocarbons emissions. Emissions of SO_x and particulates are not affected by this mode of operation.

Residue catalytic cracking (RCC) is basically the same process as FCC. Due to the higher coke laydown on the catalyst as a result of the heavier feeds, the heat balance around the regenerator may require additional measures for catalyst cooling. As the heavier feed normally has a higher metal content, especially Ni and V, the catalyst deactivation rate is so fast that the catalyst needs to be removed continuously, to be replaced by fresh catalyst. Increasing rates of fresh catalyst addition induces higher entrainment rates due to fines present in the fresh catalyst, as well as due to fines produced by attrition. Therefore, higher particulate emissions from the regenerator are expected and should be taken into account in the choice and size of the flue-gas PM abatement technique to be implemented.

Two-stage regenerator processes are tolerant of feedstocks with high Conradson Carbon Residue (CRR) values (3 – 10 % w/w) and containing high levels of metals (Ni, V and Na). The first regenerator burns 30 – 70 % of the coke and essentially all the hydrogen in it. Regeneration conditions are kept mild and vanadium on the catalyst cannot form V₂O₅. In the second regenerator, full catalytic activity is restored by completely removing the remaining coke in a dry atmosphere, as hydrogen has been previously removed. V₂O₅ is now formed at high temperature, but as there is little moisture available to form vanadic acid the catalyst is preserved. The two-stage regeneration system allows a R2R resid cracker RCC to operate at

significantly higher metal levels on the catalyst, thereby reducing the catalyst make-up requirements and operating costs.

In Thermofor Catalytic Cracking (TCC), the preheated feedstock flows by gravity through the catalytic reactor bed. The vapours are separated from the catalyst and sent to a fractionating tower. The spent catalyst is regenerated, cooled, and recycled. The flue-gas from regeneration is sent to a carbon monoxide boiler for heat recovery.

In the moving bed process, oil is heated to 400 – 700 °C and is passed under pressure through the reactor, where it comes into contact with a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated. The catalyst is regenerated in a continuous process. Some units also use steam to strip the remaining hydrocarbons and oxygen from the catalyst before the catalyst is fed back to the oil stream. In recent years, moving bed reactors have largely been replaced by fluidised bed reactors.

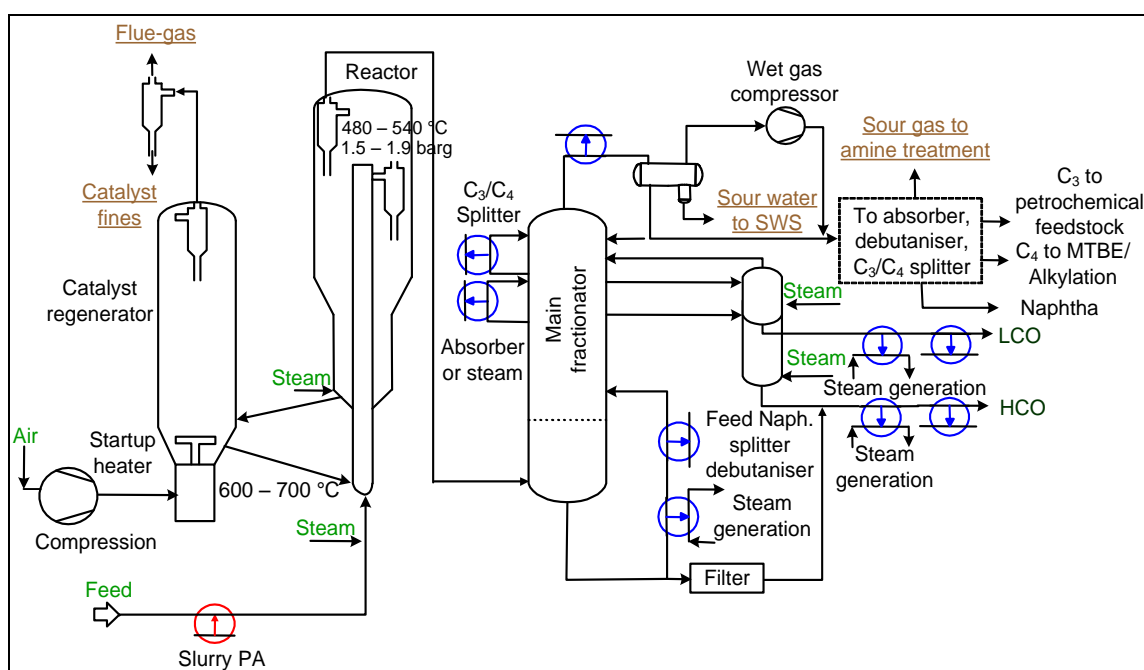


Figure 2.6: Simplified process flow scheme for a fluid catalytic cracker

Reference literature

[9, Kootungal 2008], [76, Hydrocarbon processing 2011].

2.6 Catalytic reforming

Purpose and principle

The heavy naphtha leaving the hydrotreating units is a very poor gasoline blend component due to its low octane. The purpose of a catalytic reformer is to upgrade the octane of these streams for use as a gasoline blendstock. The burning characteristics (octane number) of heavy naphtha are improved significantly by catalytic reforming. The most important characteristic of the reformate product is the octane number. Octane numbers are very low for n-paraffins, slightly better for naphthenes and isoparaffins and are highest for aromatics. There are four major types of reactions which occur during the reforming processes:

- dehydrogenation of naphthenes to aromatics
- dehydrocyclisation of paraffins to aromatics
- isomerisation
- hydrocracking.

Because the EU gasoline market is in decline and reformulated specifications (see Table 1.9) limit the allowable amount of benzene and aromatics in gasoline, catalytic reformer operation is driven more by hydrogen production needs for diesel production than to produce additional aromatics and gasoline blend components, which has traditionally been the case.

Feed and product streams

The typical feedstocks to catalytic reformer units are the hydrotreated straight-run heavy naphtha from the crude distillation unit and, if applicable, the hydrotreated heavy naphtha stream from the hydrocracker unit or coking unit, and the medium catalytically cracked naphtha stream from a FCC unit. A catalytic reformer produces hydrogen, which is essential for use in hydrotreaters (Section 2.13) and may be used in hydrocracking processes. Products from a reformer include, in addition to the hydrogen: refinery fuel gas, LPG, isobutene; n-butane and reformate. The reformate may be blended to gasoline or further separated into components as chemical feedstocks like benzene, toluene, xylene, and naphtha cracker feeds.

Some catalytic reformers operate under more severe conditions, resulting in an increased aromatics content in the reformate product.

Process description

Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulphur, nitrogen and metallic contaminants. The catalysts used in catalytic reforming processes are usually very expensive (containing platinum [Pt]) and extra precautions are taken to ensure that catalyst is not lost. There are several catalytic reforming processes in use today. In general, they can be classified into three categories: continuous, cyclic or semi-regenerative, depending upon the frequency of the catalyst regeneration. The fixed bed or moving bed processes are used in a series of three to six reactors.

Continuous catalytic regeneration (CCR) reforming process

In this process, the catalyst can be regenerated continuously and maintained at a high activity rate. The ability to maintain a high catalyst activity and selectivity by continuous catalyst regeneration is the major advantage of this type of unit. Figure 2.7 shows a simplified process flow diagram of a continuous catalytic reformer.

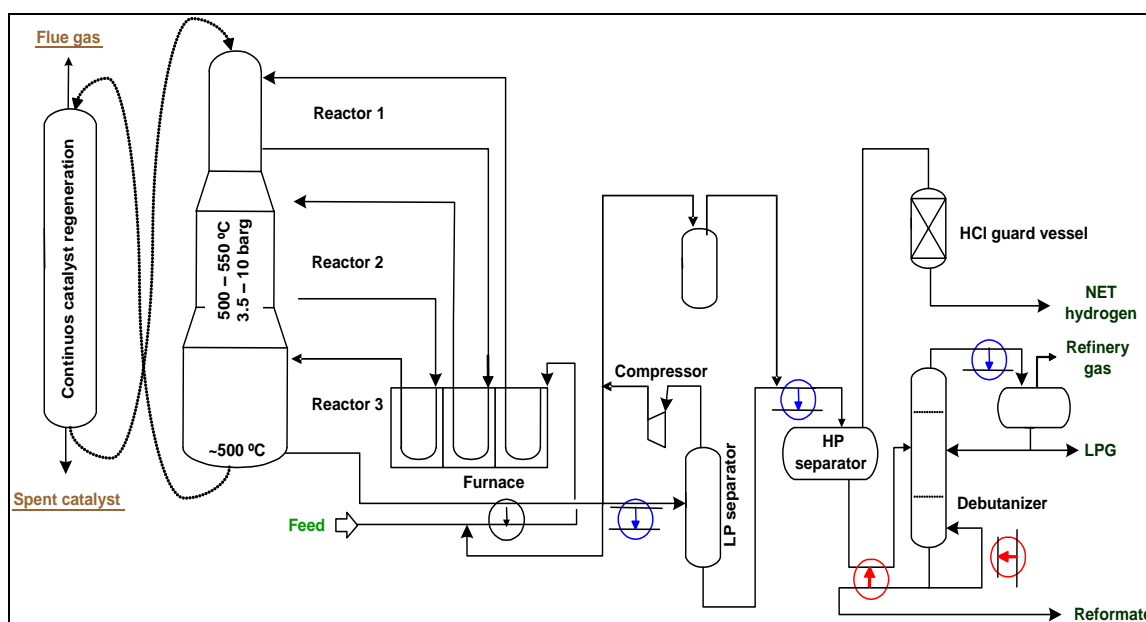


Figure 2.7: Simplified process flow scheme for a continuous catalytic reformer

Interheaters are needed between the reactors to provide the heat required for the endothermic dehydrogenation reaction. As the naphtha feed charge proceeds through the reactors, the reaction rates decrease and the reheat needed lessens. Freshly regenerated catalyst is introduced at the top of the first reactor and flows by gravity from top to bottom. From here it is passed on to the next reactor. Partially aged catalyst is removed from the bottom of the lowest reactor and sent to an external regenerator, where the carbon is burnt from the catalyst. The catalyst is acidified and reduced before being returned to the lead reactor. The reaction mixture from the last reactor is used to preheat the fresh feed and further cooled down prior to being fed to the low-pressure separator. There the hydrogen-rich gas is separated from the liquid phase. The gas is compressed and partially recycled to the naphtha feed. The remaining vapour is then further compressed, recontacted with the liquid from the low-pressure separator, cooled and fed to the high-pressure separator. The recompression and recontacting is included to maximise recovery of the C_3/C_4 fraction from the hydrogen-rich gas stream. Any excess of this hydrogen-rich gas is routed to the refinery hydrogen system to be used in hydrogen-consuming units like hydrotreaters. The selection of the reformer operating pressure and the hydrogen/feed ratio form a compromise between maximum yields and the coking rate.

The CCR reforming process has a higher energy efficiency per tonne of desired product than the semi-regenerative process, due to better yields and improved heat recovery from the products. As the CCR process is the latest and most modern type of catalytic reformer process, it has generally a design with a higher heat integration than the semi-regenerative process and leads to a higher energy efficiency. Appropriate revamping of semi-regenerative units can also achieve higher energy efficiency through the same recovery from products, from pumparounds and from integration with the topping and vacuum.

The use of a CCR generates more dioxins than a semi-regenerative process during the regeneration of the catalyst. For more information, see Section 3.6.

Operational data

This technique operates at lower pressures (3.5 – 10 bar) than, and at the same temperature as, semi-regenerative processes. It uses mono (Pt) or bi-metallic catalysts (Pt-Re, Pt-Sn). Hydrogen is also produced in these processes. A continuous regeneration reformer produces around 350 Nm^3 of hydrogen per tonne of feedstock. Since the increased coke laydown and the thermodynamic equilibrium yield of reformat are both favoured by low-pressure operation, the ability to maintain a high catalyst activity and selectivity by continuous catalyst regeneration is the major advantage of the continuous process.

Disadvantages of the CCR reforming process include its ability to make reformates with high aromatic contents >70 % v/v and that CCR reformer reformates tend to be higher boiling compared to the semi-regenerative reforming process. These qualities can impact blending CCR reformer reformates into the gasoline pool with gasoline specification of less than 35 % v/v aromatics. Compared to the other reforming technologies, much of the value from CCR reforming is the improved yields at high octanes; however, with biofuels blending and decreasing octane demand, the economics for converting other reforming technologies to CCR reforming technology is diminishing.

Economics

As an example, the investment costs based on a 3 975 m³/d continuous octanising unit (battery limits, erected cost, 1998 Gulf Coast) were 10 000 USD per m³/d.

The erected costs of a 3 180 m³/d unit (4Q95, US Gulf Coast) were USD 48.3 million (USD 15 200 per m³/d). In addition, catalyst costs add another USD 2.6 million.

Example plant(s)

Nowadays, only continuous catalytic reformer units are built. New reforming units larger than 15 000 bpd (2 400 m³/d) are typically designed as continuous catalyst regeneration reformer units. Smaller reformer units may be of continuous catalyst regeneration or semi-regenerative designs, but the cost of the CCR can become prohibitive with smaller scale units.

Reference literature

[77, REF TWG 2010], [175, Meyers 1997], [183, HP 1998], [207, TWG 2001].

Cyclic reforming process

The cyclic reforming process is characterised by having a swing reactor in addition to these on-stream, in which the catalyst can be regenerated without shutting the unit down. When the activity of the catalyst drops below the desired level, this reactor is isolated from the system and replaced by the swing reactor. The catalyst in the replaced reactor is then regenerated by introducing hot air into the reactor to burn the carbon from the catalyst. Typically, one reactor is always being regenerated.

Semi-regenerative reforming process

In this process design, regeneration requires the unit to be taken off-stream. Depending upon the severity of operation, regeneration is required at intervals of 3 to 24 months. The control of the dosage of a chlorine-containing compound to feed and operating pressures are utilised to minimise coke laydown and the associated loss of catalyst activity. The dosing rate depends on the water content of the feed (actual and potential) and the desired steady-state chloride level on the catalyst.

The reactors operate at temperatures in the range of 400 – 560° C and pressures in the range of 15 – 35 bar. This type of process produces between 130 Nm³ and 200 Nm³ of hydrogen per tonne of feedstock.

Economics

The erected cost of a semi-regenerative unit of 3 180 m³/d is USD 33 million (USD 10 400 per m³/d). In addition, catalyst costs add another USD 3.4 million (1995 - US Gulf Coast).

Many applications exist in Europe, as well as in the rest of the world.

Cross-media effects

In semi-regenerative reforming, the unit catalyst is regenerated at intervals of 3 to 24 months, depending on the intensity of the process. The emission factor of dioxins per tonne of feedstock is much lower than with continuous regeneration. For more information, see Section 3.6.

2.7 Coking processes

Purpose and principle

Coking is a severe thermal cracking process used primarily to reduce the refinery production of low-value residual fuel oils and transform them into transportation fuels, such as gasoline and diesel. As part of the process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities. When high-quality coke is required (e.g. to produce anodes for the metals industry), green coke needs to be processed in a calciner.

Feed and product streams

As the coking process is a thermal destruction process, the quality of the feed in terms of metal content, Concarbon number and other contaminants is not critical. As a matter of fact, coking is predominantly used when the feed has a high Concarbon number and contains high quantities of impurities which cannot be handled in catalytic conversion processes. All this produces high feedstock flexibility. The feed to a delayed coking unit can consist of atmospheric residue, vacuum residue, shale oils, tar sands, liquid and coal tar, which results in a petroleum coke used for fuel applications. Aromatic oils and residues such as heavy cycle oils from a catalytic cracking unit and thermal tars are suitable feedstocks for the production of needle coke and anode coke. The feed to a fluid coker is the vacuum residue, sometimes mixed with refinery sludges, tar sands, bitumen and other heavy residues.

The products from the coking fractionator are refinery fuel gas, LPG, naphtha and light and heavy gas oils. Petroleum coke is another product, with the type depending upon the process used, operating conditions and feedstock used. Coke produced by the coker is called 'green' coke and still contains some heavy hydrocarbons left from incomplete carbonisation reactions.

Process description

Two types of coking processes exist: the delayed and fluid coking processes that produce coke and the flexicoking process that gasifies the coke produced in a fluid coking process to produce coke gas.

Delayed and fluid coking

The basic process is the same as thermal cracking (Section 2.22), except that feed streams are allowed to react for longer without being cooled. Figure 2.8 shows a simplified process flow diagram of the delayed coking unit.

The delayed coking feed stream of residual oils is first introduced to a fractionating tower, where residual lighter materials are drawn off and the heavy ends are condensed (not shown in Figure 2.8). The heavy ends are removed, heated in a furnace and then fed to an insulated vessel called the coke drum, where the cracking takes place. In the case of fluid coking, a fluidised bed is used. Temperature (440 – 450 °C), pressure (1.5 – 7.0 barg) and recycle ratio are the main process variables which contribute to the quality and yields of delayed coking products. When the coke drum is filled with product, the feed is switched to an empty parallel drum (dotted drum in Figure 2.8).

When the coke drum is full, steam is then injected to remove hydrocarbon vapours. The coke bed is then quenched with water and the cokes are cut out with high pressure water. The cutting water passes to dedicated settlement where coke solids settle out and the clarified water is recycled. The wet green coke is conveyed to designated open stockpiles, where water drains out and is recycled. Green coke can already be sold and used for energy production. The yield of delayed coking is usually above 80 % (25 – 30 % coke, 65 – 75 % light products) conversion of feed to products. The production of petroleum coke is of the ratio of 0.13 tonnes of petroleum coke produced per tonne of feedstock.

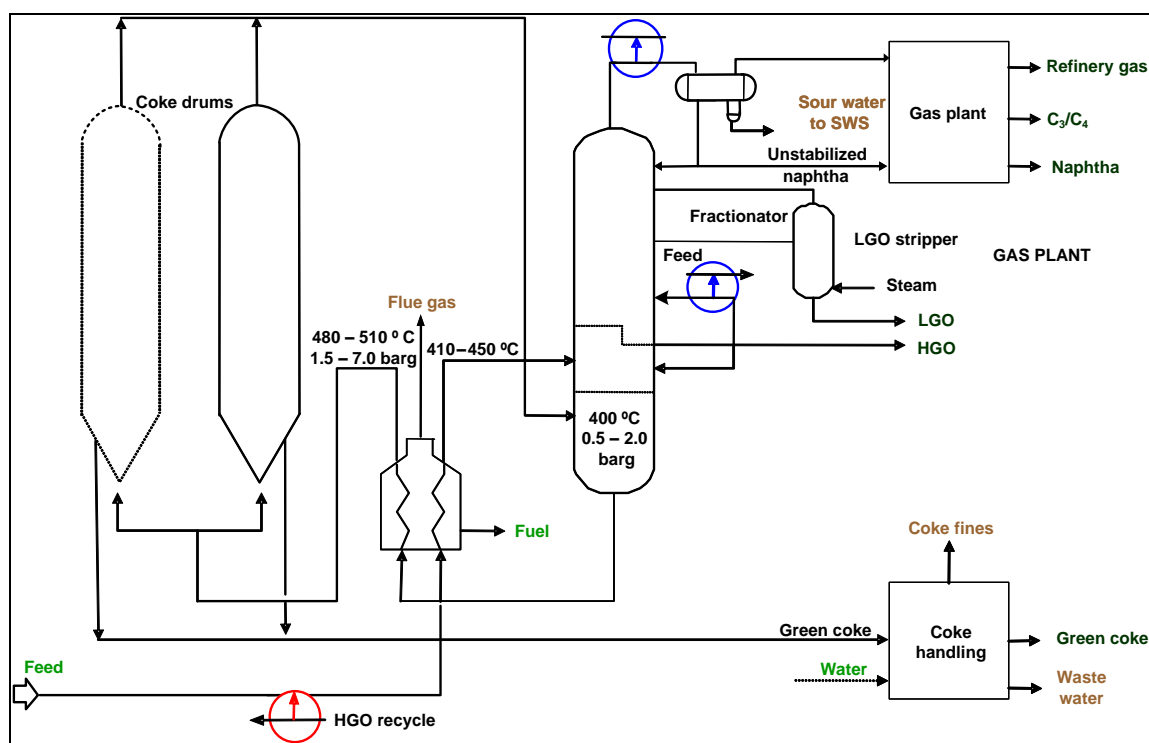


Figure 2.8: Simplified process flow scheme for a delayed coking unit

Hot vapours from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulphide and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products. Condensed hydrocarbons are reprocessed and collected water is reused for coke drum quenching or cutting. Any remaining vapours commonly pass to the flare system. Normally, products such as naphtha are totally fed to the naphtha hydrotreater for further processing. The heavier products are suitable feedstock for catalytic reforming after proper hydrotreatment. Light oil needs further treatment before being sent to the gas oil blending pool. The heavy gas oil is preferably sent to a hydrocracker unit (Section 2.13) for further conversion into light components. When no cracking units are available, it is blended in the heavy fuel oil pool.

Calciner

For certain applications, green coke should be calcined before being used or sold. The incinerator kilns are direct fuel gas or coke fine fired at the discharge end. The coke is calcinated at up to 1380 °C, driving off volatile matter and burning it within the kiln. Exhaust gases discharge from the feed end and are incinerated to burn off residuals and coke fines. Hot flue-gases pass through a waste heat boiler and gas cleaning by multi-cyclones. Collected fines from the cyclones are pneumatically conveyed to a silo with exit air filters. The calcined coke discharges to a rotary direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and the water scrubber. Collected cyclone fines may be recycled to product, which is oil sprayed as a dust suppressant, or may be incinerated or sold as a fuel.

Flexicoking

The flexicoking process typically converts 84 – 88 % w/w of the vacuum residue to gaseous and liquid products. Virtually all metals in the feed are concentrated in the solids purged from the process (1 – 4 % w/w of the fresh feed). Flexicoking is a very robust process in which coking and gasification are fully integrated. The process is advanced compared to the classic delayed coker in terms of operation and labour intensity. [276, Kamienski et al.2008]

The flexicoking process uses three major vessels: the reactor, the heater and the gasifier. As auxiliary facilities, the system includes a heater overhead cooling system and a fines removal system, a coke gas sulphur recovery unit and reactor overhead scrubber (Figure 2.9). The

preheated vacuum residue feed is sprayed into the reactor, where it is thermally cracked, typically at 510 – 540 °C. The freshly formed coke is deposited on the surface of the fluidised recirculated coke particles. In the gasifier, the coke is reacted at elevated temperatures, typically 850 – 1 000 °C, with air and steam to form coke gas, a mixture of hydrogen, carbon monoxide and dioxide and nitrogen. Sulphur in the coke is converted in the gasifier primarily to hydrogen sulphide, plus traces of carbonyl sulphide (COS). Nitrogen in the coke is converted to ammonia and nitrogen. Unlike normal gasifiers which are fed with pure oxygen, the flexicoking gasifier is fed with air, resulting in a coke gas with a relatively low calorific value, as it contains a high quantity of inert nitrogen.

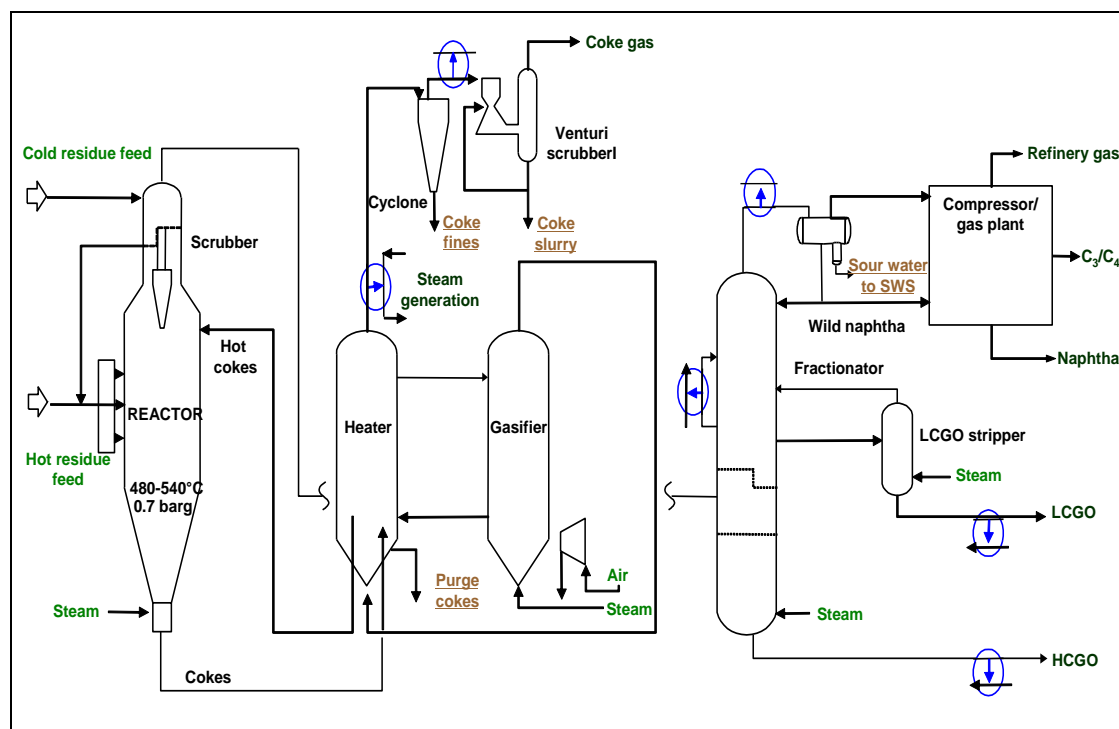


Figure 2.9: Simplified process flow scheme for a flexicoker

The cracked hydrocarbon vapour product from the reactor is passed through cyclones to remove coke particles and is subsequently quenched in a scrubber section located at the top of the reactor. Material boiling above 510 – 520 °C is condensed in the scrubber and recycled to the reactor. The lighter material goes overhead to conventional fractionation, gas compression and light ends recovery sections. The treatments and use of the products are very similar to the ones already described in the delayed coker. Pressure relief from the fractionator of the coking processes passes to flare and from the coke drums to the quench tower system.

2.8 Cooling systems

Under the IPPC process, a horizontal BREF on Industrial Cooling Systems [69, COM 2001] was produced that covers many topics of relevance to the refineries sector. To avoid repetition, therefore, this section on cooling addresses only topics not covered by that horizontal BREF. Moreover, some cooling water pollution issues have already been studied in the OSPAR (North Sea) and HELCOM (Baltic) processes.

Purpose and principle

In a refinery, the cooling of feed and product streams is required to allow refinery process operations to take place at the right temperatures, and to bring products to their appropriate storage temperature. Even though heat integration of process systems ensures that significant cooling can be achieved by exchanging heat between streams to be cooled and streams to be heated, additional cooling is still required. This additional cooling should be provided by an external cooling medium: water and/or air.

Process description

A wide range of techniques is used for cooling purposes in oil refineries. Most refineries use a combination of the techniques available. The selection of a cooling system depends on the required cooling temperature, the cooling capacity, contamination risk (primary or secondary cooling loop) and local circumstances. A simplified diagram of the cooling techniques is shown in Figure 2.10 and briefly described below.

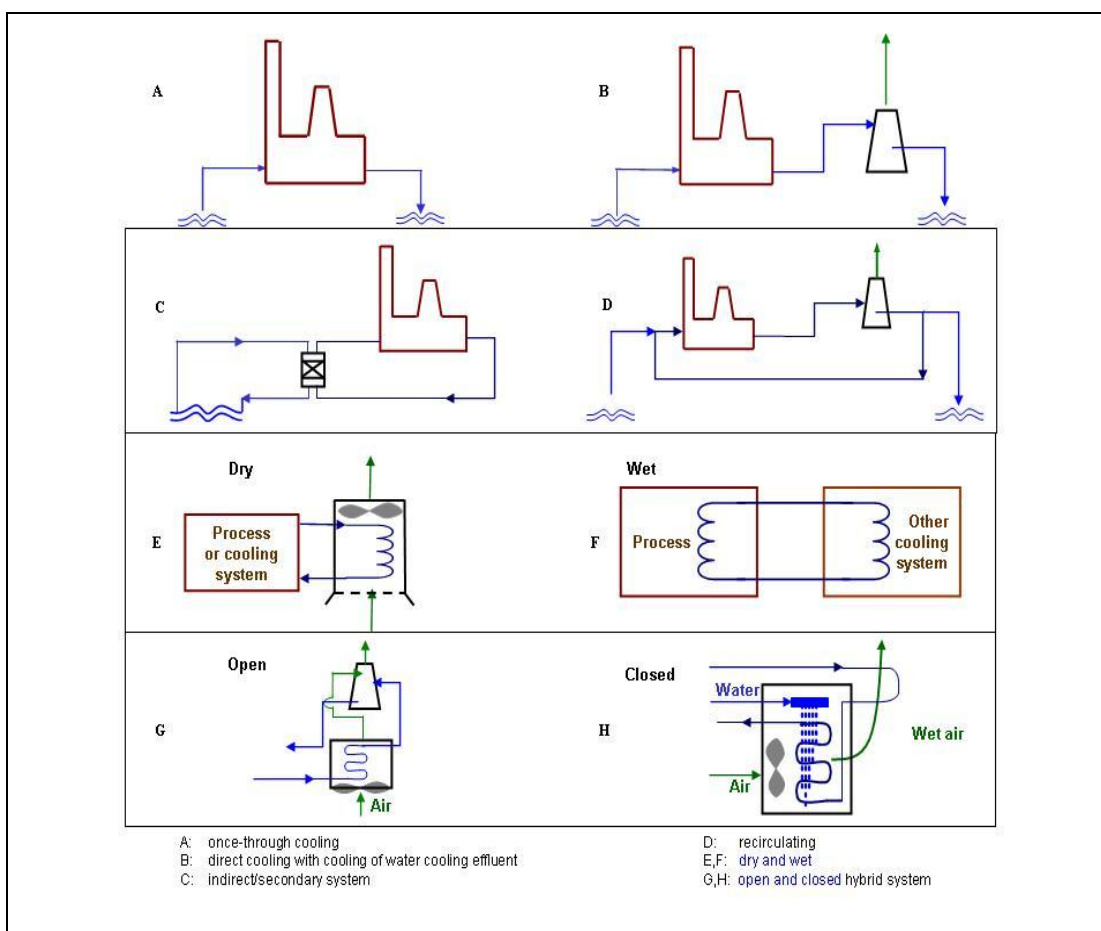


Figure 2.10: Simplified diagrams of the cooling systems used in refineries

Air cooling

In an air cooler (forced or induced draught), the process stream in the tubes is cooled against the air delivered by a fan. An induced draught air cooler is illustrated in Figure 2.10.

Direct water cooling (i.e. quenching)

Because of the high contamination generated by this type of cooling, quenching is only used in cokers (Section 2.7), in gasifiers and in some sludge incinerators.

Once-through system (seawater, river water, etc.)

In a typical once-through cooling system, water is extracted from a surface water body, filtered if necessary and sometimes treated with biocide to inhibit fouling. It is then passed around the refinery to enable cooling through heat exchangers. The cooling water is passed through a process unit once and is then either treated or discharged directly into the receiving environment without treatment. There are several ways to use water for once-through cooling in refineries and that carry a different risk of contamination by process streams as described below:

- Once-through cooling water used for cooling non-polluting streams, e.g. in power generation. A cooling tower system is generally applied when the thermal loading of the surface water is too high (see Figure 2.10 A and B).
- Once-through cooling water used for heat exchange with a recirculating water system which then cools the process streams (Figure 2.10 C).
- Once-through cooling water is used to cool process streams directly (via heat exchangers) (see Figure 2.10 A and B).

Circulation system (tempered water, cooling water)

In this system, most cooling water is repeatedly recycled through cooling towers using ambient air. In order to control the concentration of contaminants and the solids content in the cooling water, a blowdown stream is used, which is sent to the waste water treatment unit, and make-up water is added. A certain amount of water also exits the system through evaporation (Figure 2.10 D).

Wet closed system (normally water)

Tempered water is used when process streams to be cooled should not be exposed to the (low) cooling water temperatures (Figure 2.10 F).

Hybrid systems

In these hybrid systems, both air and water are used as the cooling media. These systems normally maximise the use of air cooling and the rest is done by water cooling. Two types of systems are available and they are shown in Figure 2.10 G and H.

Refrigeration systems

In specific cases where for safety reasons process streams have to be cooled below ambient temperatures, refrigeration systems are applied. This can be either a direct refrigeration system, i.e. using the refrigerant (propane or ammonia) in the process, or an indirect system (Figure 2.10 F) using a circulation system (e.g. brine, glycol) where the refrigerant cools the circulating liquid.

2.9 Desalting

Purpose and principle

Crude oil and heavy residues can contain varying quantities of inorganic compounds, such as water-soluble salts, sand, silt, rust and other solids, together characterised as bottoms sediment. The salt in the crude is primarily in the form of dissolved or suspended salt crystals in water emulsified with the crude. These impurities, especially salts, can lead to fouling and corrosion of heat exchangers (crude preheaters) and especially the crude distillation unit overhead system (Section 2.19). Salts are detrimental to the activity of many of the catalysts used in the downstream conversion processes. Additionally, sodium salts stimulate coke formation (e.g. in furnaces). Some inorganic impurities are chemically bound, such as vanadium and nickel, and are often referred to as oil-soluble salts. These cannot be eliminated in a desalter. Moreover, excess water has to be removed from crudes with high water content. Therefore, desalting of the incoming crude oil is generally applied before separation into fractions (See Section 2.19).

The principle of desalting is to wash the crude oil or heavy residues with water at high temperature and pressure to dissolve, separate, and remove the salts and other water extractable components.

Feed and product streams

Crude oil and/or heavy residues (oily feedstock) and reused and fresh water are the feed streams to the desalter with desalted crude oil and contaminated water (brine) being the outputs of the desalting processes. The water phase from the crude distillation unit overhead and other used water streams are normally fed to the desalter as wash water. Efforts are made in the industry to minimise the water content of the desalted crude to less than 0.3 % and bottoms sediments to less than 0.015 %. The concentrations of inorganic impurities in the cleaned stream are highly dependent on the design and operation of the desalter, as well as on the crude source.

Process description

After preheating to 115 – 150 °C, the oily feedstock is mixed with water (fresh and reused water) in order to dissolve and wash out the salts.

Intimate mixing of the oil and wash water takes place in a globe valve mixer, a static mixer or a combination of both. The water must then be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals to assist in breaking up the emulsion and, in addition, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets.

The separation efficiency depends on pH, density and viscosity of the crude oil, as well as on the volume of wash water used per volume of crude. Either AC or DC fields may be used and potentials from 15 kV to 35 kV are used to promote coalescence. Many refineries have more than one desalter. Multiple-stage desalters also exist. The wash water containing dissolved hydrocarbons, free oil, dissolved salts and suspended solids is further treated in an effluent treatment plant (Section 4.24). Where bottoms sediments are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids. Figure 2.11 shows a simplified process flow diagram of a modern design crude desalter.

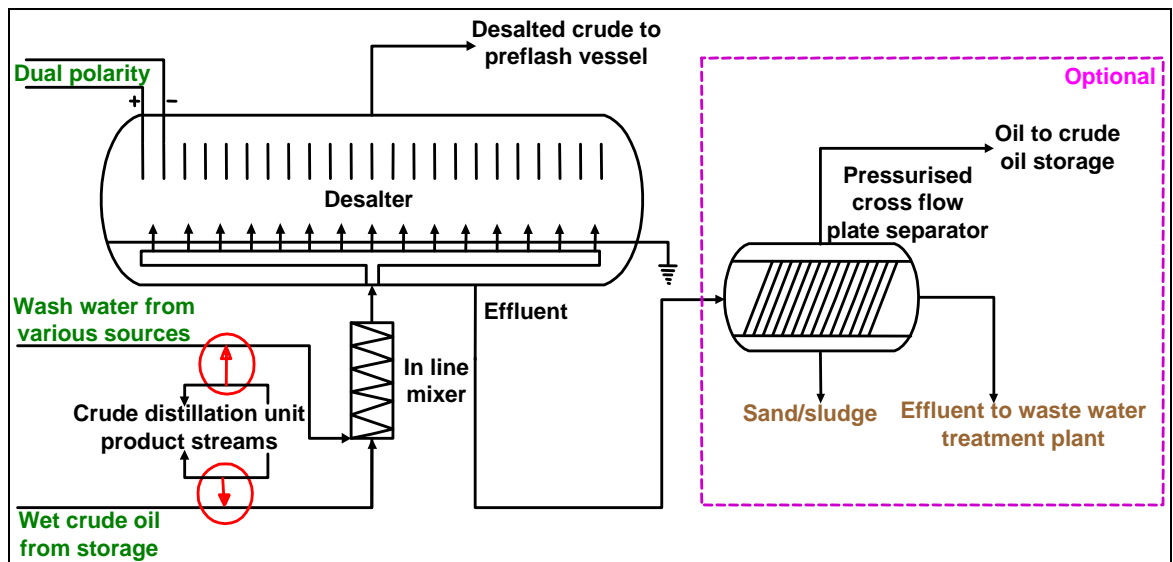


Figure 2.11: Simplified flow diagram of a crude desalter

2.10 Energy system

Heat-producing plants are an essential and integral part of most refining processes/activities. An important aspect of the refining energy system is the effective use of internal residue streams as part of the energy mix. This chapter describes some principles of energy production and management in the context of refinery fuels.

Purpose and principle

Heat and electricity are needed to run a refinery. The extensive heat requirement is provided by fuel combustion either directly (by heaters, furnaces) or indirectly via steam. Steam is usually produced inside the refinery. This is increasingly coupled to the generation of electricity in surplus because it can be sold on the external market (as with steam if there is local demand).

An emerging proposition is full commercialisation where (some) steam and electricity production is outsourced to a power company specialist. Some refineries have switched to importing their base load steam and electricity needs from third party companies based locally.

Fuels and fuel systems

The fuel required for the production of steam and power or for the firing of the furnaces originates either from fuels that are produced by the refinery itself (refinery fuels) or from natural gas that is bought outside, or a combination of both. Normally, most or even all of the gaseous and liquid refinery fuels used are by-products of refinery processes. The composition and quality of these fuels vary with the crude oils processed. The refinery fuel pool is a careful balance between energy required, type of crude processed, emission limits and economics.

Refinery fuel gas (RFG)

The majority of the fuel used in a refinery is refinery fuel gas (RFG). This is a mixture of methane, ethane, ethylene and hydrogen and may contain some CO and small amounts of C₃, C₄, N₂ and H₂S. RFG is produced and collected in the refinery gas system, but has to be used quickly and cannot normally be sold as a product. The composition may change over time depending on refinery operations and the feedstock being processed and will be different from site to site, again depending on the feedstock and installed plants, for example if the refinery has a coker that supplies syngas (CO + H₂) to the RFG system.

Most refinery fuel gas systems have alternative sources of supply: refinery gas, imported gas (normally natural gas) and liquefied petroleum gas (LPG). External supplies usually become part of the RFG system, although dedicated units may run on commercial fuel. RFG, if properly treated, is a low-polluting fuel. More information on RFG is provided in Section 4.10.2.

These gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking, coking and all hydrodesulphurising processes). In the latter case the gas streams are normally treated by amine scrubbing to remove H₂S before being released to the refinery fuel gas system, and dust removal and COS conversion if necessary (Section 4.23). Coke gas forms a main refinery gas source if coking takes place in the refinery. Sulphur content in the form of H₂S is normally below 100 – 220 mg/Nm³, and will strongly depend on the pressure used in the amine treating units. Levels of 4 – 40 mg/Nm³ are possible for gas treated at high pressure (20 bars), and lower levels, 2 – 15 mg/Nm³, can even be reached with very high pressure (50 bars). Residual H₂S concentrations achievable by using a refinery fuel gas treatment are shown in Table 4.80 of Section 4.23.5.1. The nitrogen content is negligible.

Fuel gas system

Figure 2.12 shows a schematic diagram of a typical fuel gas system. The fuel gas is supplied from the different refinery units. In this diagram, backup supply is provided by imported natural gas and by internally produced LPG, which is vaporised and routed into the fuel gas header. The condensation of heavier hydrocarbons and/or water is critical for the fuel gas system. Normally all units have their own fuel gas knockout drum, in which condensate formed in the fuel gas

distribution system is separated. The fuel gas lines from this drum need to be steam-traced to avoid condensation in the supply lines to the individual burners. Liquids from the fuel gas knockout drum are drained to a closed slops system.

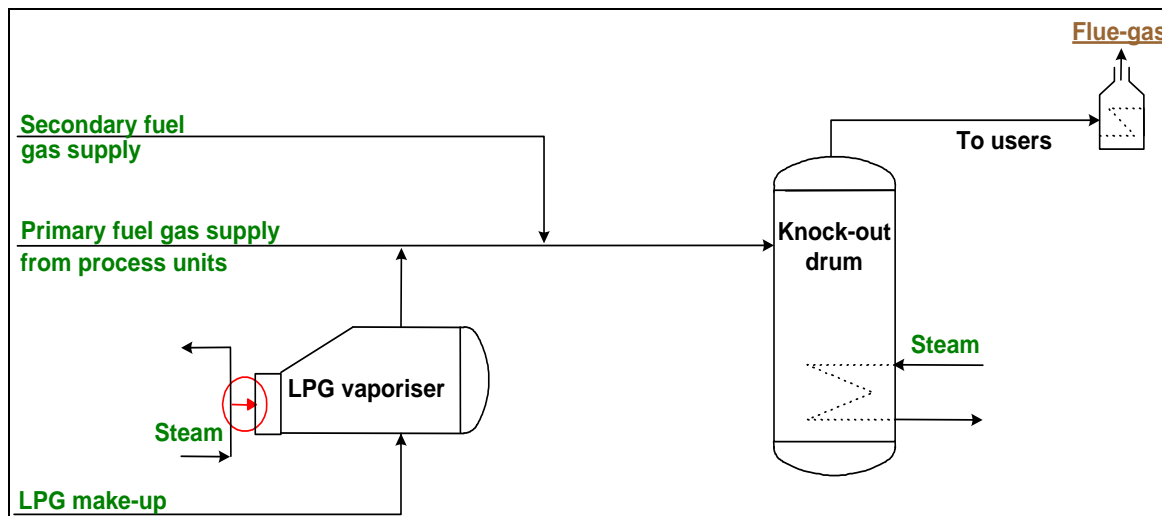


Figure 2.12: Simplified flow diagram of a fuel gas system

Liquid refinery fuel

Heavy fuel oil (HFO) used in the refinery is normally a mixture of the residues from atmospheric and/or vacuum distillation and conversion and cracking processes. Liquid refinery fuels are available in various grades, viscosity being the main parameter. The lower the viscosity, the more expensive the fuel. The heavier (more viscous) grade fuels require heating to reduce their viscosity before combustion. They contain sulphur (<0.1 – 6 %), metals (e.g. V, Ni) and nitrogen (0.1 – 0.8 %) resulting, after direct combustion, in high SO₂, particulates and NO_x emissions. They can also be gasified in the Integrated Gasification Combined Cycle (IGCC) plant, where virtually any refinery residue (e.g. visbroken or thermal tars) can be converted to heat and power.

Provided that the crude oil is properly desalted, the ash content of the fuel will be directly related to the total solids, the amount being proportional to the sum of the nickel and vanadium present (Ni-V value: 0.03 – 0.15 % w/w, depending on the residue source and crude origin). To arrive at the metal content of the HFO, the metal content of the crude is multiplied by a factor of 4 – 5 (dependent on the yield of residue and the residue content of the crude). The metal content of the HFO can vary between 40 ppm and 600 ppm for HFO from a North Sea crude and Arabian Heavy crude, respectively, generating particulate concentrations in the flue-gas of 150 – 500 mg/Nm³. The most prominent metals indigenous to the crude are vanadium and nickel, other metals such as cadmium, zinc, copper, arsenic and chromium have also been detected [150, Dekkers, Daane 1999]. Table 2.2 shows the metal contents of residual fuel oils typically used in refineries.

Table 2.2: Metal content of residual oil

| Metal | Concentration range (ppm) | Average concentration (ppm) |
|-------|---------------------------|-----------------------------|
| V | 7.23 – 540 | 160 |
| Ni | 12.5 – 86.13 | 42.2 |
| Pb | 2.49 – 4.55 | 3.52 |
| Cu | 0.28 – 13.42 | 2.82 |
| Co | 0.26 – 12.68 | 2.11 |
| Cd | 1.59 – 2.27 | 1.93 |
| Cr | 0.26 – 2.76 | 1.33 |
| Mo | 0.23 – 1.55 | 0.95 |
| As | 0.17 – 1.28 | 0.8 |
| Se | 0.4 – 1.98 | 0.75 |

Source: [234, HMIP UK 1995]

Liquid refinery fuel system

As has already been stated, liquid refinery fuels are heavy residues that should be stored in a separate storage tank at an elevated temperature to reduce the high viscosity. A typical refinery fuel oil system (schematic diagram, see Figure 2.13) includes a dedicated mixing tank (normally off-site), a circulation pump and a heater (when required). The system discharges fuel oil at a constant pressure and at the required conditions of temperature and viscosity, so that atomisation and efficient combustion are possible. If the fuel consumption is low, the cost of installing heated storage, preheating, etc. may not be justified for the use of heavy fuels and so a light fuel oil will be used. Liquid refinery fuels are normally used for process start-ups.

Solid fuels

Solid fuels such as petroleum coke can be gasified as a refinery fuel gas source for refineries (Flexicoking, Section 2.7). Coke is burnt in the catalytic cracking regenerator (Section 2.5) and in the coking process and represents a heat production source in the refinery. Coal, as imported fuel, is not applied in European refineries.

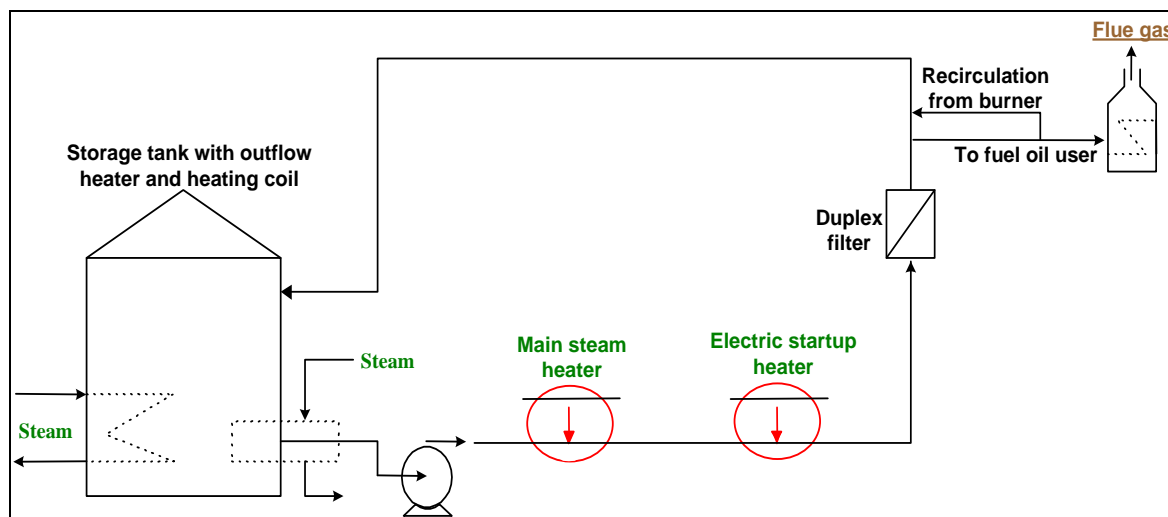


Figure 2.13: Simplified flow diagram of a heavy fuel oil system

Energy production techniques

This section is not intended to include a detailed description of energy production techniques (steam and power), since this is covered in the LCP BREF [7, COM 2006].

Furnaces and boilers

Many of the individual refinery processes and utility systems combust fuel (gas and/or liquid) in dedicated furnaces and boilers to supply the heat necessary for the process. Fired process heaters and boilers are the main heat producers. The former transfer the heat released in the combustion process directly to the process stream and the latter produce steam that will be used somewhere in the refinery. The principle of steam generation is the heating of boiler feed water, under pressure in a specified fuelled boiler or a waste heat boiler consisting of heat exchanger bundles (economisers and superheaters). In this document, no distinction is made between furnaces and boilers, except when relevant.

A variety of furnaces and burner types are used in refineries, largely determined by the heat-release characteristics required by a particular process. Many but not all furnaces are dual (oil/gas) fired to allow flexibility in the refinery fuel system. Refinery process heaters are typically rectangular or cylindrical enclosures with multiple-fired burners of specialised design using mainly low combustion intensity. Boilers (fixed or fluidised bed) are generally fairly standard steam-producing units of medium or high combustion intensity. Waste heat boilers may also be present in the furnaces of stacks. Well maintained and operated direct-fired heaters and boilers achieve thermal efficiencies of over 85 %. If air preheat is applied and the combustion products (flue-gas) are cooled close to their dew point, the thermal efficiency can be as high as 93 %. Boilers consume about 10 – 20 % of refinery energy requirements.

Gas and steam turbines

Gas turbines work as follows: fresh air at ambient conditions is drawn into the compressor where its temperature and pressure are raised. The high-pressure air proceeds into the combustion chamber, where the fuel is burnt at a constant pressure. The resulting high-temperature gases then enter the turbine where they expand to atmospheric pressure, thus producing power. Steam turbines are used to transform the steam pressure to power. Combined cycle processes combine the gas and steam turbine processes to produce power at higher efficiency than is reached with open-cycle turbines (steam and gas). More information about gas and steam turbines, as well as combined cycles, can be found in the LCP BREF [7, COM 2006].

Cogeneration plants (CHP)

These systems are designed for the co-production of heat and power. The fuel for this type of facility is usually natural gas. It is, however, also possible to fire refinery gas as part of the fuel slate, thus potentially reducing the amount of refinery gas available for combustion in boilers and furnaces. The steam and power cogeneration concept can also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high-pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Integrated gasification combined cycle (IGCC)

Integrated gasification combined cycle is a technique for producing steam, hydrogen (optional) and electrical energy from a variety of low-grade fuel types with the highest conversion efficiency possible. During the gasification of the oil with oxygen and/or air, syngas is also produced and used for energy production, typically in a combined cycle for the production of heat and electricity. Hydrogen can also be separated from the syngas for use in the refinery (Section 2.14).

The principle is based on the high-temperature and high-pressure reaction of organic carbons or coke with steam and understoichiometric amounts of oxygen (partial oxidation) to produce syngas ($\text{CO}+\text{H}_2$). After the combustion chamber, the system contains a number of sophisticated energy recovery systems to produce steam and electricity. Figure 2.14 shows a block flow diagram of an IGCC plant. In the partial oxidation of hydrocarbons, the product gas contains a certain amount of free carbon (soot). The soot particles are removed from the gas together with the ash in a two-stage water wash.

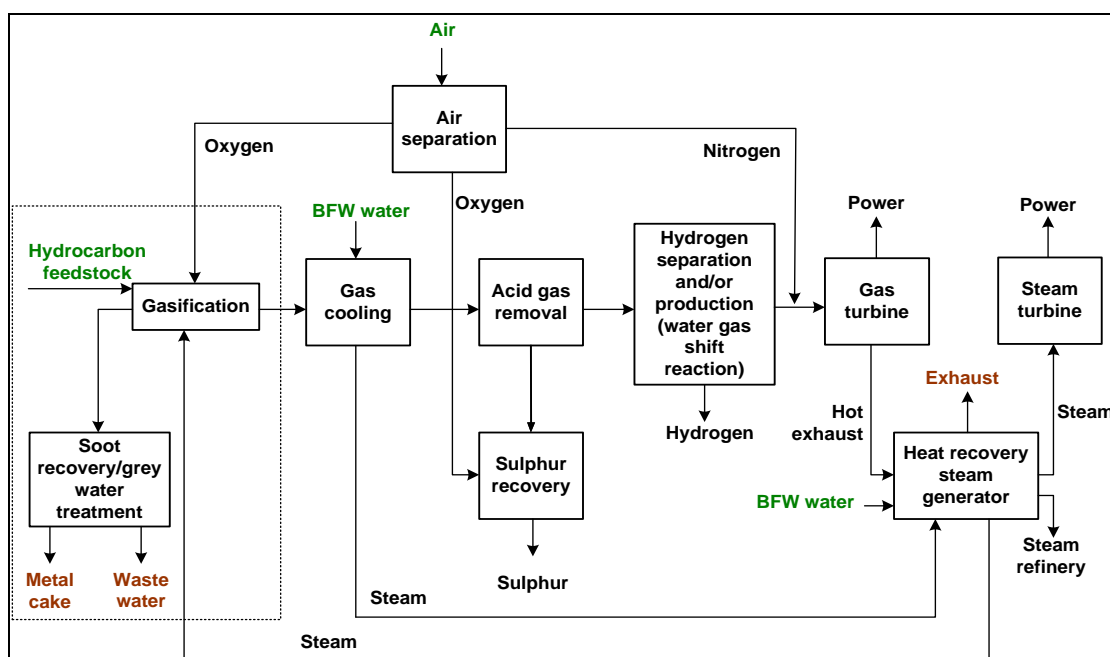


Figure 2.14: Block flow scheme for an IGCC process

The gasification plant consists of two integrated complex units. In the first, syngas manufacturing process plants (SMPP), the gasification of heavy fractions takes place and the syngas is produced and purified. In the second, i.e. the combined cycle power plants, the syngas is fed to a combined cycle thermoelectric unit. The SMPP includes the two sections described below.

- **Gasification and carbon extraction:** in the gasification section, the feedstock is gasified through a non-stoichiometric reaction with pure oxygen and water; the reaction occurs in the gasifier, a non-catalytic vessel internally coated with refractory, operating at a high temperature (about 1 300 °C) and pressure (about 65 bar).
- **Gas cooling and purification:** in the gas-cooling section, the waste heat from syngas is recovered by the generation of steam at three pressure levels. A small quantity of carbon, formed in the gasifiers is removed from the gas by direct contact with water in a scrubber. Water is then treated in the grey water treatment and then sent to the existing refinery biotreatment plant. A solid effluent in the form of a filter cake is discharged from this unit and sent to external plants for the recovery of the metals. In addition, a COS hydrolysis reactor is provided to convert the small amount of COS produced in the gasifier to H₂S. This section also includes a gas expander for the recovery of the pressure energy of the syngas (pressure in gasifiers is about 65 bar). This system contains an acid gas removal process which consists of a circulating amine stream used to selectively absorb the H₂S formed in the gasifier and during the COS hydrolysis. It also contains an air separation unit. This unit produces the oxygen required for the gasification and the Claus plant, and the nitrogen for syngas conditioning. It is based on conventional cryogenic air fractionation. And finally, it contains a sulphur recovery unit where Claus units recover elemental sulphur from the H₂S recovered in the acid gas removal section. This, along with a tail gas treatment section, maximises the overall sulphur recovery.

After the cooling and purification sections, the purified syngas is sent to the combined cycle power plant, for power generation. This mainly consists of a conventional cycle with a gas turbine, a heat recovery steam generator and a steam turbine.

Products from the energy system

As mentioned at the beginning of this section, the energy system of a refinery is there to provide the heat and power necessary to carry out the process. A short description of the types of products produced by the energy system of a refinery (steam and power) is given below.

Steam

The different steam qualities generated in the boilers of the refinery have the general characteristics described below (the heat content ranges from about 2 700 MJ/t for low-pressure steam to 3 200 MJ/t for superheated high-pressure steam at 50 bar):

- High-pressure (HP) steam network (>30 bar, 350 – 500 °C), generated in waste heat boilers (cooling of hot off-gases and/or hot products in catalytic processes and hydrocrackers) and in fired boilers. HP steam is mainly used in turbines to produce electrical power (and medium-pressure steam).
- Medium-pressure (MP) steam network (7 – 20 bar, 200 – 350 °C), generated by pressure reduction of HP steam, is used within the refinery for stripping, atomisation, vacuum generation and heating (e.g. reboilers, tanks).
- Low-pressure (LP) steam network (3.5 – 5 bar, 150 – 200 °C), generated in heat exchangers by cooling of hot products, and by pressure reduction of MP steam. LP steam is used for heating, stripping and tracing.

Steam is produced by heating demineralised water, ‘boiler feed water’ (BFW), under pressure in a steam boiler. Steam-raising plants are normally fuelled with refinery fuel gas or liquid. The refinery is equipped with dedicated steam boilers in virtually all process units, containing a HP-, MP- and LP-steam distribution network and with HP-, MP- and LP-condensate collection networks, which are connected with the BFW preparation unit and the condensate storage tank. (Reference is made to Figure 2.15 and to the LCP BREF [7, COM 2006].

Steam used in turbines and heaters after cooling is usually recovered as condensate. BFW is therefore a mixture of fresh demineralised make-up water (quality dependent on steam pressure) and recovered condensate. BFW make-up can be brought in but can also be prepared at the refinery using drinking water, filtered groundwater, seawater distillation, surface water or even treated effluent by using a combination of treatment operations, such as sand filtration or microfiltration (to remove suspended solids) and demineralisation which is accomplished by subsequent cation and anion exchange (see dotted area in Figure 2.15). Reverse osmosis (to remove ions, colloids and large organic molecules) is usually applied in new plants and is followed in some cases by mixed bed ion exchange and active carbon filtration for final polishing. The condensate tank is generally equipped with an oil detection system and an oil skimming device. To avoid corrosion in the steam and condensate systems, oxygen and carbon dioxide are removed in deaerators, and oxygen scavengers and corrosion inhibitors are added. After conditioning, the BFW is pumped to the boilers. In boilers, the hot flue-gases and BFW flow countercurrently; BFW is preheated in the economiser and further heated in the first and second superheater. In order to keep the concentration of dissolved compounds and suspended solids in the steam drum constant, a condensate blowdown of 1 – 2 % is normally required.

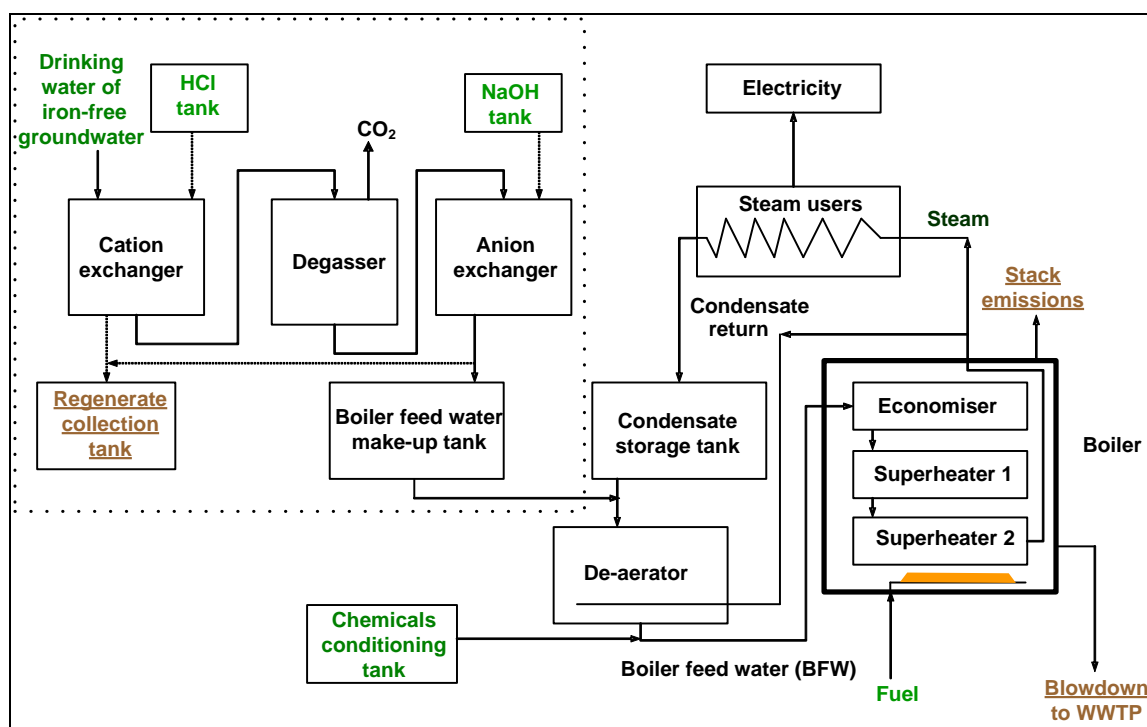


Figure 2.15: Typical layout of a boiler feed water preparation unit and a steam boiler

Electrical power

Power is mainly generated in turbines with high-pressure steam but can also be produced in gas turbines on site and/or bought from the grid (e.g. hydrogenerated power). Electricity is necessary to run pumps, compressors, control systems, valves, etc. Refinery electrical systems are therefore extensive.

Energy management

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal aim is to continuously match the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This issue is also analysed in this document and Section 2.15 examines the integration of all techniques that may be used in a refinery. This section is included here because the energy efficiency of a refinery can be increased not only by improving the energy efficiency of the individual processes (which is addressed in each section) or energy efficiency of the energy production system but also by improving energy management, energy conservation and heat integration/recovery within the refinery as a whole.

Energy management has long been an important issue for refineries. For example, management techniques such as the ISO 14000 system series, the EN 16001 System or EMAS can provide an appropriate framework to develop suitable energy management systems and can increase the energy efficiency of the refinery as a whole. Energy conservation techniques such as reporting and giving incentives for energy savings, carrying out combustion improvements or reviewing the energy integration of the refinery are some of the techniques that may have a great impact on reducing energy consumption and consequently on increasing the energy efficiency of a refinery. Other technical tools to increase efficiency are the heat integration/recovery techniques, of which examples are: the installation of waste heat boilers, the installation of expanders to recuperate power and increasing the insulation of buildings and process units to reduce heat losses. Steam management is another good tool for increasing energy efficiency.

2.11 Etherification

Purpose and principle

A number of chemicals (mostly alcohols and ethers) are added to motor fuels either to improve performance or to meet environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels, reduce carbon monoxide generation and reduce atmospheric ozone due to the lower reactivity of resulting VOC emissions. The octane improvement has been a factor in the phase-out of lead as a fuel additive as required by the Auto-Oil I programme. As a result, a number of different ethers are currently added to the gasoline and are better able to meet both the new oxygen requirements and the vapour pressure limits. The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME). Some refineries manufacture their own supplies of these ethers.

Feed and product streams

Isobutylene and/or isoamylene and methanol (or ethanol) are necessary to produce MTBE (or ETBE) and/or TAME. Isobutylene is obtained from a number of refinery sources including: the light naphtha from the FCC and coking units; the by-product from steam cracking of naphtha processes or light hydrocarbons during the production of ethylene and propylene; catalytic dehydrogenation of isobutane and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides. These processes are described in the LVOC BREF [85, COM 2003]. Methanol (or ethanol) comes from an external supply.

Process description

Multiple variations of commercial processes are available. Most processes can be modified to react isobutylene or isoamylene with methanol or ethanol to produce the corresponding ether. All use an acidic ion exchange resin catalyst under controlled temperature and pressure conditions. Temperature control of the exothermic reaction is important to maximise conversion and minimise undesirable side effects and catalyst deactivation. The reaction is usually carried out in two stages with a small excess of alcohol to achieve iso-olefin conversions of over 99 % and the methanol consumption is essentially stoichiometric. The basic difference between the various processes is in reactor design and the method of temperature control.

MTBE production process

Figure 2.16 shows an example of a simplified process flow diagram of an MTBE plant. The feed stream is cooled prior to entering the top of the primary reactor. The resin catalyst in the primary reactor is a fixed bed of small beads. The reactants flow down through the catalyst bed and exit the bottom of the reactor. Effluent from the primary reactor contains ether, methanol and unreacted iso-olefin and usually some paraffins from the feed. A significant amount of the effluent is cooled and recycled to control the reactor temperature. The net effluent feeds to a fractionator with a section containing catalyst or to a second reactor. Ether is withdrawn as the bottom product, and unreacted alcohol vapour and iso-olefin vapour flow up into the catalyst reaction to be converted to ether. The process usually produces an ether stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling. The excess methanol and unreacted hydrocarbons are withdrawn as net overhead product, and fed to a methanol recovery tower. In this tower, the excess methanol is extracted by contact with water. The resultant methanol-water mixture is distilled to recover the methanol, which is then recycled to the primary reaction.

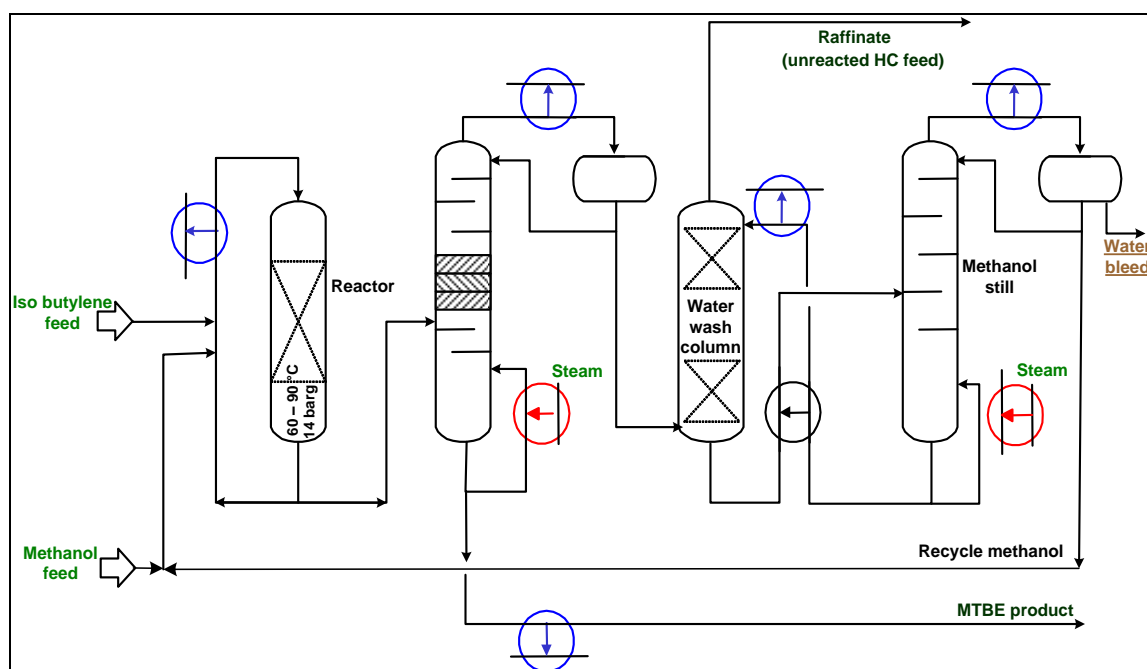


Figure 2.16: Simplified process flow scheme of a MTBE production process

ETBE production process

The MTBE unit is able to produce ETBE with minor modifications and elimination of bottlenecks (increase capacity of the column and cooler, increase bottom temperature in catalytic column, change top and bottom temperature in ethanol/water column).

TAME production process

In this process, C_5 isoamylenes are separated from the light catcracked spirit stream (LCCS) from the FCC unit and catalytically reacted with methanol in the presence of hydrogen to produce TAME. The main stages for TAME production are pentane removal, scavenging, reaction and purification. Figure 2.17 shows a simplified scheme for TAME production.

C_5 removal is achieved by distillation (depentaniser) of the LCCS feedstock. Overheads are condensed and the hydrocarbons are returned as reflux while gases go to the refinery flue-gas system. A C_5 side-stream is withdrawn from the column as feed to the TAME unit. Column bottom liquids (C_{6+}) are routed to re-blending with the eventual product from the TAME unit.

The C_5 stream is then scavenged to remove catalyst poisons by passing it through an ion exchange resin to remove basic nitrogen compounds, e.g. ammonia, and any metallic contamination. A hydrogen feed is also scavenged to remove any acidic components. The feedstock, containing injected methanol and hydrogen, is fed to the reactor section. Hydrogen is used to convert dienes into mono-olefins and prevent gum formation during the reaction. This takes place over a palladium-impregnated ion exchange resin and the isoamylenes are converted to TAME.

The TAME product stream is purified by fractional distillation, washing and phase separation. Fractionator overheads pass to a reflux drum with the gaseous phase of low-boiling hydrocarbons (C_1 , C_2 , C_4 , etc.) together with unreacted hydrogen before being vented to refinery fuel gas or flare. The bottom product of TAME gasoline with some methanol is cooled and mixed with recycled water from the methanol recovery plant, then routed to a settler for phase separation. The TAME gasoline fraction from this is blended with the depentaniser bottoms C_{6+} stream and passed to storage. The methanol/water fraction is recycled to the methanol recovery plant feed drum.

Methanol is recovered by distillation in a common still, with the overhead's methanol being condensed and passed to buffer storage for recycling to the TAME plant or other uses. The bottoms are essentially water with some contaminants and are mainly recycled with a purge to effluent treatment to avoid formic acid build-up.

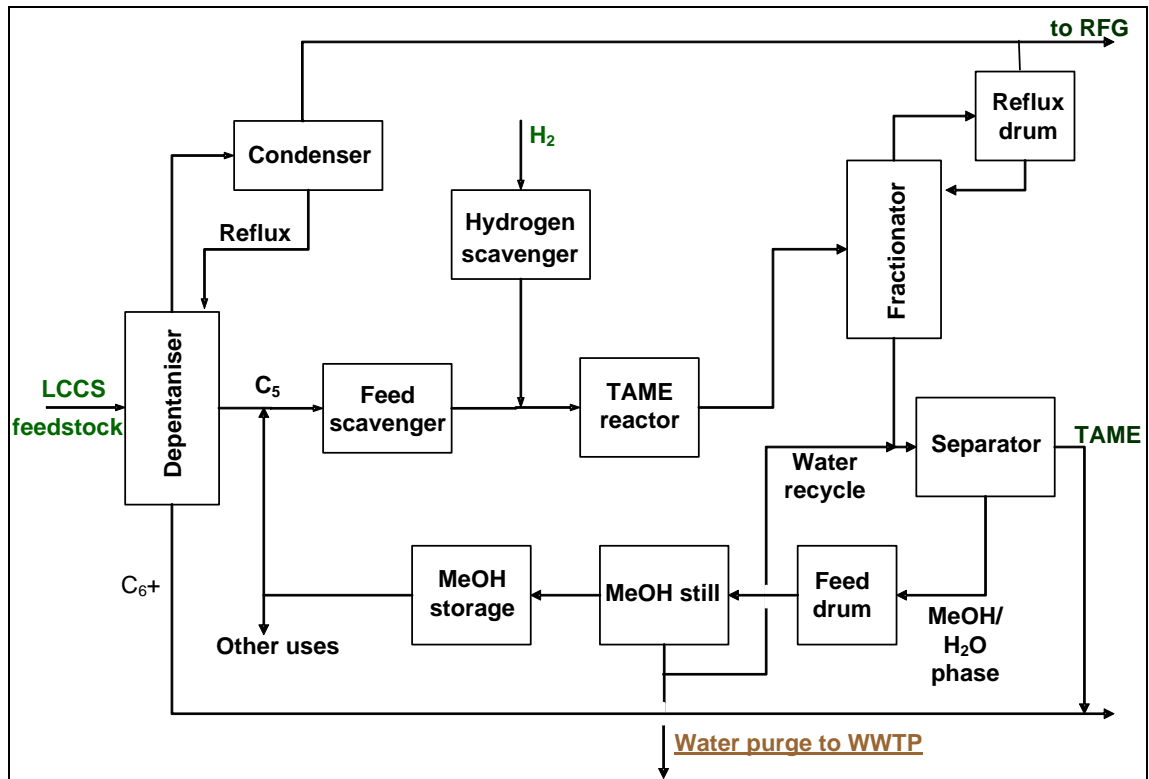


Figure 2.17: Simplified process flow scheme of TAME production

2.12 Gas separation processes

Purpose and principle

Low-boiling hydrocarbons are usually treated in a common separation plant operating at elevated pressures. The purpose of a gas plant is to recover and to separate $C_1 - C_5$ and higher compounds from various refinery off-gases by distillation. In mineral oil refineries, one (or more) gas plant is present to handle different gas streams from different processes. (e.g. cat reformers, catalytic crackers, distillation units). These plants are the core for installations refining natural gas (Section 2.17), where the different components are separated. Depending on application of the products, some refineries remove mercury from LPG, tops and naphtha.

Feed and product streams

The feed of the gas plant consists of gas and liquid streams from crude distillation, cat crackers, catalytic reformers, alkylation, desulphurisation and similar units. Pretreatment of some feedstocks may be necessary, typically by hydro-desulphurisation (Section 2.13) or amine treating (H_2S removal, see Section 4.23.5.1). The compounds recovered depend on the composition of the feed and the market requirements. The gas streams are normally separated into C_1 and C_2 fractions for sale or use as refinery fuel gas, LPG (propane and butane) and a light gasoline (C_5 and higher) stream. Olefins, isoparaffins and n-paraffins can be also separated in the process.

Process description

As a minimum, the gas plant consists of two columns where the first one, an absorber/stripper column (de-ethaniser) strips all light C_2 -minus components to maximise recovery of C_3 -plus components from the feed streams. Figure 2.18 shows a simplified process flow diagram of a gas plant.

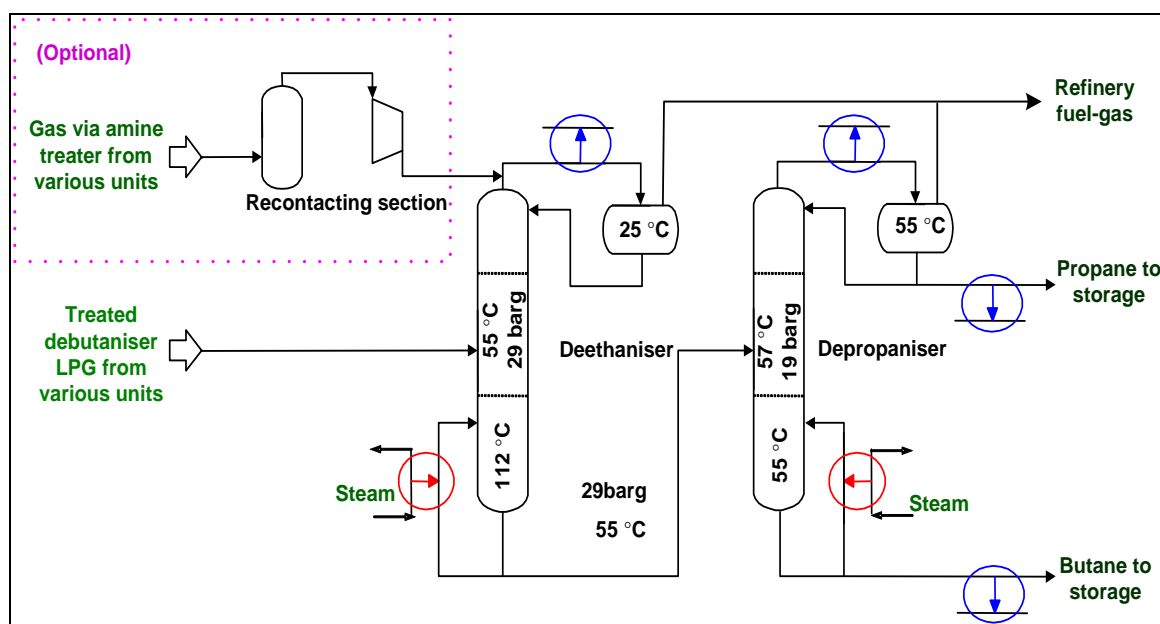


Figure 2.18: Simplified process flow scheme for a part of a gas plant

The feed stream to the gas plant is cooled and chilled, the residual vapour phase from this being routed to a refrigerated absorber, meeting chilled recycled light gasoline absorbent. The absorber overhead is the C_1, C_2 fraction. The bottoms are combined with the liquid stream from chilling, and pass to the first fractionator or de-ethaniser. The first fractionator overheads (essentially C_2 -ethane) are combined with the absorber overheads while the bottoms pass to the second fractionator to produce a C_3/C_4 overheads stream and debutanised gasoline bottoms. A recontacting section, where vapours from various units are compressed and recontacted with the

de-ethaniser overhead, can be installed to maximise the C_3/C_4 recovery. The bottoms of the de-ethaniser column, mainly C_3/C_4 compounds, are fed to the depropaniser column. This overheads stream is routed to a third fractionator to split the C_3 and C_4 streams as overheads (propane) and bottoms (butane), respectively. Products pass to pressurised storage via any final sweetening by selective molecular sieve adsorption. Subsequent loading of transport containers is carried out by means such as closed-loop systems or by venting and release to the refinery fuel gas system.

The gasoline bottom stream passes to a fourth fractionator to produce a depentanised fraction for use as chilled, recycled gasoline on the absorber. The net output is blended to form the gasoline product. A drying step before sending to storage may be necessary (not shown). Also, a vessel containing a bed of caustic pellets (not shown) can be installed in the butane system as an additional guard, although water and H_2S should have been removed in the top of the de-ethaniser and de-propaniser column. If no (or insufficient) upstream treatment has taken place, this can also be done in the unit itself, e.g. with an amine H_2S absorber followed by a mercaptan oxidation/extraction of the de-ethaniser bottoms with amine H_2S absorption of the de-ethaniser net overhead gas.

If thermal and/or catalytic cracking units are present, recovery of olefinic components may also be worthwhile. It is also possible to separate isobutane from n-butane. The isobutane can be used as feed to an alkylation unit, while the n-butane (or part of it) can be used as a blending component in the gasoline pool or isomerisation.

2.13 Hydrogen-consuming processes

Two types of processes are included in this section: hydrocracking and hydrotreatments. Both processes take place over a metal catalyst in a hydrogen atmosphere. Many of these processes are found in a refinery, normally named according to the type of feed to treat and the reaction conditions. The common denominator to these processes is that all rely on hydrogenation processes and consequently consume hydrogen. Isomerisation processes of alkanes or olefins also consume some hydrogen, but these processes are included in a separate section (Section 2.16).

Purpose and principle

Hydrotreating and hydroprocessing

Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulphur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter, more saleable products. Both processes are usually placed upstream of these processes in which sulphur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units. The processes use catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen.

Hydrotreating

Hydrotreating can be divided into a number of reaction categories: hydrodesulphurisation, hydrodenitrification, saturation of olefins and saturation of aromatics. A hydrotreater unit specifically employed to remove sulphur is usually called a hydrodesulphurisation unit (HDS). In this section the standard hydrotreating of naphtha, mid-distillate and residue-type feed streams is discussed and includes the items described below.

- A naphtha hydrotreater unit normally serves three purposes: desulphurisation, denitrogenation and stabilising the naphtha feed stream to the downstream isomerisation and reformer units. Stabilising the naphtha streams usually requires the conversion of unsaturated hydrocarbons produced in thermal and catalytic cracking processes into paraffins. The selective hydrogenation of light dienes that are contaminants of many light olefin streams may also be partially hydrogenated. Hydrogenation of aromatics is a variant of either naphtha or of processed distillate. Gasoline desulphurisation is dominated by sulphur removal from FCC naphtha, which accounts for about 35 % of the gasoline pool but over 90 % of the sulphur in gasoline. Deep reduction of the gasoline sulphur (to below 10 ppm) must be made without decreasing the octane number or losing gasoline yield. The problem is complicated by the high olefins contents of FCC naphtha, which contributes to octane number enhancement but can be saturated under HDS conditions.
- A mid-distillate hydrotreater unit normally has two purposes: desulphurisation and hydrogenation of the mid-distillate stream. Stabilising mid-distillate streams is required when large quantities of cracked components are blended to the mid-distillate pool, and usually requires partial saturation of aromatics and olefins and a reduction of the N content. The full saturation of aromatics may be required to prepare naphtha, kerosene, and diesel feedstocks. Among the applications of this process are smoke-point improvements in aircraft turbine fuels, reduction of the aromatic content of solvent stocks to meet requirements for air pollution control, production of cyclohexane from benzene (LVOC) and cetane number improvement in diesel fuels.
- Diesel oil deep desulphurisation (Hydrofining) is normally done to heating and diesel oils to meet product sulphur specifications. Large decreases of diesel sulphur require a high desulphurisation of 4,6-dimethyldibenzothiophene, as this is the least reactive sulphur compound that has substitutions on both 4- and 6-positions. The deep HDS problem of

diesel streams is exacerbated by the inhibiting effects of co-existing poly-aromatics and nitrogen compounds in the feed, as well as H₂S in the product.

- Residue hydrotreating is mainly applied to improve the residue feed quality (normally atmospheric residue) to a residue catalytic cracker (RCC) unit. RCCs are restricted to process residue streams by their metal content and Concarbon number.

Hydroprocessing

Hydroprocessing may also be designed to remove low levels of metals from the feed. The metals to be removed include nickel and vanadium, which are native to the crude oil, as well as silicon and lead-containing metals that may be added elsewhere in the refinery.

Hydrocracking

Hydrocracking is one of the most versatile of all refining processes, capable of converting any fraction, from atmospheric gas oils to residual (deasphalted) oil, into products with a lower molecular weight than the feed. The hydrocracking reactions occur under high hydrogen partial pressure in the presence of a catalyst with a two-fold function: hydrogenation and cracking. Hydrocracking may also be used for the cracking of superior fuels and the production of lubricants (dewaxing is discussed in Section 2.3). The type of catalyst maximises the production of naphtha, mid-distillates or lube production. The presence of hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products, giving net products, which are a mixture of pure paraffins, naphthenes and aromatics. Hydrocracking produces mid-distillates with outstanding burning and cold flow properties as follows:

- kerosene with low freezing points and high smoke points;
- diesel fuels with low pour points and high cetane numbers;
- heavy naphthas with a high content of single-ring hydrocarbons;
- light naphthas with a high isoparaffin content;
- heavy products that are hydrogen-rich for feed FCC units, ethylene plants (LVOC), or lube oil dewaxing and finishing facilities (Section 2.3).

When hydrocracking is applied to heavy residues, a pretreatment is needed to remove high metal contents before the hydrocracking reaction is produced. Residue hydroconversion is a type of hydrocracking applied to convert low-value vacuum residue and other heavy residue streams into lighter low-boiling hydrocarbons by reacting them with hydrogen.

Feed and product streams

Hydrotreating and hydroprocessing

These processes are applied to a wide range of feedstocks, from LPG up to heavy residue and mixtures thereof. Table 2.3 summarises the feeds, products and process objectives for each type of hydrotreatment.

Table 2.3: Feedstocks, desired products and process objectives of hydrotreatments

| Feedstocks | Desired products | For the removal of: |
|-----------------------------------|--|---------------------------------------|
| LPG | Clean LPG | S, olefins |
| Naphthas | Catalytic reformer feed (S: 0.05 – 0.5 % w/w) | S (<0.5 ppm), N, olefins |
| LPG, naphthas | Low diene contents | Dienes (25 – 1 ppm) in product |
| Cat. cracked naphtha | Gasoline blending component | S |
| Atmospheric gas oils | Ethylene feedstock (LVOC) | S, aromatics |
| | Jet | S, aromatics |
| | Diesel | S, aromatic and n-paraffins |
| Vacuum gas oils | Ethylene feedstock | Aromatics |
| | Kerosene/jet (S: 0.05 to 1.8 % w/w) | S, aromatics |
| | Diesel (S: 0.05 to 1.8 % w/w) | S, aromatics |
| | FCC feed | S, N, metals |
| | Low-sulphur fuel oil | S |
| | Lube oil base stock | Aromatics |
| Atmospheric residue | FCC feedstock | S, N, CCR ^(*) , and metals |
| | Low-sulphur fuel oil | S |
| | Coker feedstock | S, CCR, and metals |
| | RCC feedstock | CCR, and metals |
| (*) CCR=Conradson Carbon Residue. | | |

Hydrocracking

Hydrogen in substantial quantities is consumed in these processes, making the hydrogen manufacturing unit mandatory (Section 2.14) in refineries that contain hydrocracking. In addition to the treated products, these processes produce a stream of light fuel gases containing hydrogen sulphide, ammonia and water.

As is reflected in Table 2.4, the main feed stream to a hydrocracker is the heavy vacuum distillate stream from the high vacuum distillation unit. These feedstocks are fractions which are very difficult to crack and cannot be cracked effectively in catalytic cracking units. Other process streams such as heavy cycle oil from the catalytic cracker unit, heavy gas oils from the coker or visbreaker unit, extracts from lube oil units, mid-distillates, residual fuel oils and reduced crudes may be blended to the main heavy vacuum distillate stream. The main products are LPG, gasoline, jet fuel and diesel fuel, all practically sulphur-free. The production of methane and ethane is very low, normally less than 1 %.

Table 2.4: Feedstocks and desired products of hydrocracking processes

| Feedstocks | Desired products |
|--|---------------------------|
| Naphthas | LPG |
| Atmospheric gas oils | Naphtha |
| Atmospheric residue | Diesel |
| Vacuum gas oils | LPG |
| | Naphtha |
| | Ethylene feedstock (LVOC) |
| | Kerosene/jet |
| | Diesel |
| | Lube oil base stock |
| Vacuum residues | LPG |
| | Naphtha |
| | Kerosene |
| | Gas oil |
| | Fuel oil |
| Tars and derived bitumens (metal content <500 ppm) | Diesel |

Process description

Types of reactor technologies applied in hydroconversion and hydrotreatment

There are several residue hydrotreating and hydroconversion technologies in use today. They can be classified into four categories: fixed bed; swing reactor; moving bed and ebullated bed. The selection of the type of process is predominantly determined by the metal content in the feed. Fixed bed residue hydroconversion is applied for 'low' metal-containing feeds (100 ppm) and the required conversion is relatively low, moving bed or ebullated bed technology is used for 'high' metal-containing feeds. To overcome metal poisoning of the catalyst in fixed beds and to maintain the concept, some licensors propose the swing reactor concept: one reactor is in operation whilst the other one is off-line for catalyst replacement. The concept and layout of the fixed bed hydroconversion technology is identical to long residue hydrotreating. Moving bed technology or ebullated bed technology is selected when the metal content in the residue feed is typically above 100 ppm but below 500 ppm. Normally this concentration of metals in the feed is found in vacuum residue streams from heavier crudes, bitumen streams from tar sands and heavy atmospheric residue streams. Both technologies allow withdrawal and replacement of the catalyst during operation, the main difference is the reactor configuration.

Hydrotreating and hydroprocessing

Naphtha hydrotreater

Naphtha feed is mixed with a hydrogen-rich gas stream, heated and vaporised in the reactor feed/effluent exchanger and the furnace, and fed into the hydrotreater reactor with a fixed bed cobalt/nickel/molybdenum catalyst. The reactor conditions can vary but are typically 30 – 40 bar and 320 – 380 °C. The reactor effluent is cooled in the feed/effluent exchanger and reactor cooler and flashed into the high-pressure separator. The flashed vapours, consisting mainly of unreacted hydrogen, are compressed and recycled to the reactor. The fractionation part is very similar to the one explained in the hydroconversion process. (See also hydrofining below in this section.)

Catalytic distillation (CD HDS)

This process aims to selectively desulphurise (to ultra low sulphur) FCC gasoline with minimum octane loss. Hydrogen and full range FCC gasoline are fed to the reactive distillation column where light naphtha is distilled from the top. Bottoms containing the reacted mercaptans are fed to the CD HDS, where heavy and mid naphtha are catalytically desulphurised. Catalytic distillation eliminates catalyst fouling because fractionation removes heavy coke precursors from the catalyst zone. The lifetime of CD HDS is similar to FCC (4 – 5 year cycles). Milder temperature and pressure diminish octane losses.

Distillate hydrodesulphurisation

Figure 2.19 provides a simplified flow diagram of a typical distillate HDS unit. The distillate feed may range from kerosene up to long vacuum gas oil or mixtures thereof. The reactor system is in principle the same as for the naphtha hydrotreater. The main difference is that the feed does not fully vaporise and the reactor operating conditions are more severe, 40 – 70 barg and 330 – 390 °C. Furthermore, it is normal practice that wash water is injected into the reactor effluent stream when nitrogen-rich feedstocks are desulphurised.

Solid deposits like ammonium sulphides $(\text{NH}_4)_2\text{S}$ and chlorides NH_4Cl are formed in the cooler parts of the unit and must be removed by water wash. The liquid from the low-pressure separator is fed to a stripper column to stabilise and strip off the light hydrocarbons and H_2S . The stripping steam and light hydrocarbons are taken overhead, condensed and separated into a sour water phase and a hydrocarbon phase. The water phase is sent to the sour water stripper, and the light hydrocarbon phase is normally recycled to the crude unit or naphtha hydrotreater distillation section for further fractionation. Any water dissolved and dispersed in the distillate should be removed to avoid the formation of haze and ice when stored.

The wet distillate is therefore either fed to a vacuum column, where the total water content is lowered to 50 ppm, or sometimes a combination of coalescer and molecular sieve beds is used, where water is selectively adsorbed on the bed.

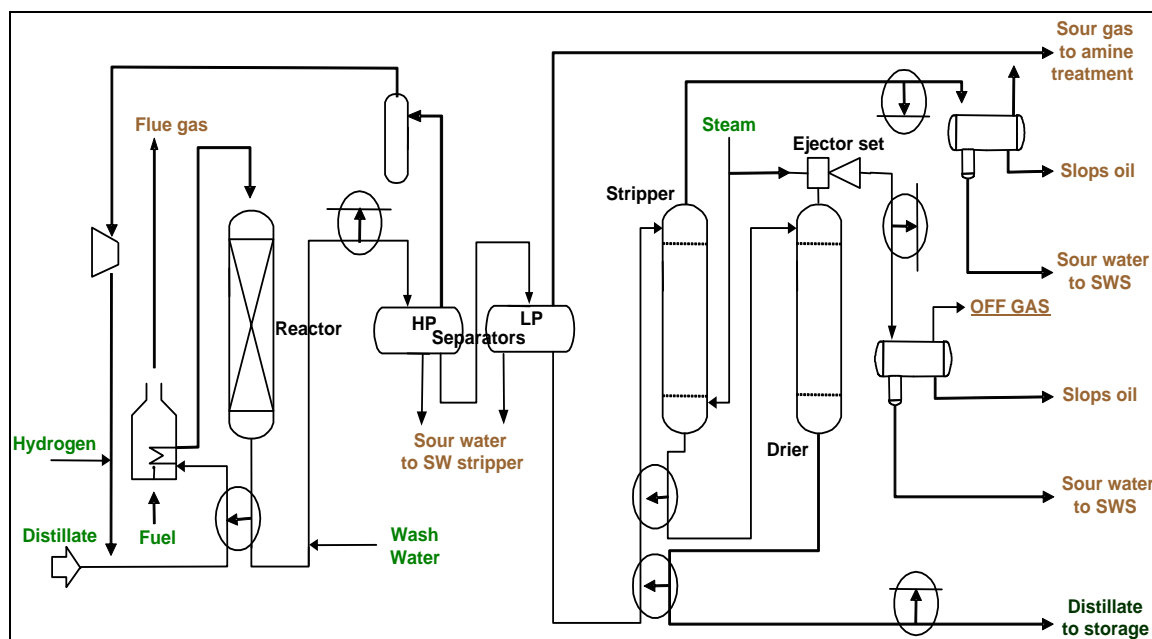


Figure 2.19: Simplified process flow scheme of a distillate hydrodesulphurisation unit

Diesel oil deep desulphurisation (hydrofining)

Because this technique operates at low pressures, efficient hydrogen utilisation can be achieved within an overall refinery context. Very low sulphur contents can be achieved (8 ppm) in the raffinate. The unit usually operates at 45 bar and consumes very small amounts of hydrogen. Equivalent deep desulphurisation techniques for gasoline with a comparatively low hydrogen consumption are currently under development.

Research on this process has gained considerable importance in recent years (further information can be found in Sections 3.13, 4.13 and Chapter 6 of this document). Development is taking place both at the research and industrial levels to deliver a wider process option. Approaches can be grouped depending on whether the technique is applied before, after or during FCC; whether it uses a large amount, average amount or no H_2 to remove sulphur species; whether it targets solely reduction of sulphur content or combines other improvement processes; and whether it is a new process or an optimisation (revamping) of HDS design or conditions.

Lower sulphur content can be achieved by revamping existing HDS units by means of replacing the catalyst type, increasing catalyst volume, enhancing operating severity (temperature and H_2 pressure), removing H_2S from recycle gas, and using high efficiency distribution trays. Commercially available catalysts are numerous and evolving, such as a new catalyst preparation method that increases active Co-Mo-S phase.

The following tables show examples of revamping process data:

Table 2.5: Revamping process examples from 500 ppm to 30 ppm sulphur

| | Current | UOP | IFP | Akzo | Criterion | Topsoe |
|---|---------|-------|-------|------|-----------|--------|
| LHSV(^o) | 2 | 1.5 | 1.45 | 1.08 | 0.5 | 1 |
| Amine scrubber installed | no | yes | yes | yes | yes | yes |
| Mol % purity of H ₂ | 75 | 90 | 91.3 | 75 | 75 | 75 |
| Ratio of circulating H ₂ | 1 | 1.9 | 3.649 | 1 | 1.6 | 1.16 |
| Catalyst packing method | Sock | Dense | Sock | Sock | Sock | Sock |
| ^(o) Liquid Hourly Space Velocity Source: [79, Fayruzov et al.2009] | | | | | | |

Table 2.6: Revamping process examples from 30 ppm to 10 ppm sulphur

| | UOP | IFP | Akzo | Criterion | Topsoe |
|--|------------|------------------|--------------|-------------|----------|
| LHSV(^o) | 1.5 to 0.9 | 1.45 to 1 | 1.08 to 0.45 | 0.5 to 0.4 | 1 to 0.7 |
| Ratio of circulating H ₂ | 1.9 to 2 | 3.649 to unknown | 1 | 1.6 to 1.85 | 1.16 |
| Partial pressure (kg/cm ²) | 46 | 58 | 46 | 46 | 46 |
| ^(o) Liquid Hourly Space Velocity Source [79, Fayruzov et al.2009] | | | | | |

New deep HDS processes focus on process and reactor design configuration as well as addressing other steps. Some examples are octane recovery, cetane increases, dearomatisation, eliminating nitrogen compounds. These new techniques are based on other principles like reactive distillation, adsorption, reactive adsorption at high temperature or polar adsorption in countercurrent approach. Some of them consume significantly low H₂ such as the reactive adsorption principle.

There has been intensive development in non-H₂ desulphurisation techniques. Most of them are mentioned in Chapter 6 of this document. Some oxidative desulphuration processes (like SulphCo) have reached commercialisation with substantially lower operating costs.

Table 2.7 illustrates some processes of deep desulphurisation of gas oil and naphtha.

Table 2.7: Examples of processes for deep gas oil and naphtha desulphurisation

| Process | Key features | Industrial application | H ₂ consumption | Octane loss | Name of process | Licensors |
|---------------------------------|-------------------------|------------------------|----------------------------|-------------|-----------------|-------------------|
| Naphtha hydro-treating (NHT) | Conventional | yes | high | high | various | a number of firms |
| NHT + octane increase | Zeolite + isomerisation | yes | high | low | Octgain, Isal | ExxonMobil, UOP |
| Selective NHT | RT-225 | yes | medium | low | SCANfining | ExxonMobil |
| | Dual catalyst | yes | medium | low | Prime-G+ | IFP |
| | Catalytic distillation | yes | medium | low | CDHydro/CDHDS | CDTech |
| Selective NHT + octane increase | Combination | yes | medium | low | SCANfining II | ExxonMobil |
| Adsorption | Zn adsorbent | yes | low | low | S Zorb | Philips |
| | Alumina adsorbent | pilot | low | low | Irvad | Alcoa |
| Extractive distillation | Selective solvent sys. | yes | none | low | GT-DeSulf | GTC |
| Oxidation | Peroxyacid | pilot | none | low | CED | Petrostar |
| | Ultrasound | pilot | none | low | SulphCo | Bechtel |
| Alkylation | Solid acid | pilot | low | low | OATS | BP |
| Bio processing | Bio catalysis | no | none | low | | Enchira |

Source: [80, Stanislaus et al.2010]

Residue hydrotreating

The principle process scheme for residue hydrotreating is the same as normal distillate. The main difference is the reactor system, which normally consists of two or three reactors in series. Removal of the metals from the residue feed normally occurs in the first reactor(s) and uses a low-activity coarser Co/Mo catalyst. Further hydrotreating and hydrogenation occur in the tail reactor(s), resulting in a higher hydrogen-to-carbon ratio and a lower Concarbon number of the residue. Since the catalysts operate in a H₂S and NH₃-rich environment the nickel/molybdenum or nickel/tungsten catalysts are usually applied in the tail reactors. Table 2.8 shows the typical hydrotreatment operating conditions for the different feedstocks.

Table 2.8: Typical hydrotreating operating conditions

| Operating conditions | Naphtha | Mid-distillate | Light gas oil | Heavy gas oil | Residuum |
|---|-----------|----------------|---------------|---------------|-----------|
| Liquid hourly space velocity | 1.0 – 5.0 | 1.0 – 4.0 | 1.0 – 5.0 | 0.75 – 3.0 | 0.15 – 1 |
| H ₂ /HC ratio, Nm ³ /m ³ | 50 | 135 | 170 | 337 | 300 |
| H ₂ partial pressure, kg/cm ² | 14 | 28 | 35 | 55 | 55 |
| Reactor temperature, °C | 260 – 380 | 300 – 400 | 300 – 400 | 350 – 425 | 350 – 425 |

Source: [175, Meyers 1997]

Hydrogenation of light dienes

This process is a highly selective catalytic process that can hydrogenate acetylenes and dienes to the corresponding mono-olefin without affecting the valuable olefin content of the feedstock. In addition, this process can be designed to provide hydro-isomerisation of some of the olefins

(e.g. conversion of 1-butene to 2-butene). Hydrogenation takes place in a liquid phase fixed bed reactor. Unless the hydrogen purity is low, no separation step is required for the removal of the light ends from the product. Thus, reactor effluent can be charged directly to downstream units.

Saturation of aromatics

The use of highly active noble metal catalysts permits the reactions to take place under mild conditions. Because of the mild conditions and the very selective catalyst, the yields are high, and hydrogen consumption is largely limited to just the desired reactions. The process is carried out at moderate temperatures (205 – 370 °C) and pressures (3 500 – 8 275 kPa) over a fixed catalyst bed in which aromatics are saturated and in which hydrogenation of olefins, naphthenic ring openings and the removal of sulphur and nitrogen occur.

Hydrocracking

Hydrocracking normally uses a fixed bed catalytic reactor with cracking occurring under substantial pressure (35 – 200 kg/cm²) in the presence of hydrogen at temperatures between 280 °C and 475 °C. This process also breaks the heavy, sulphur-, nitrogen- and oxygen-bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated and dewatered to remove impurities (H₂S, NH₃, H₂O) before being sent to the hydrocracker. If the hydrocracking feedstocks are first hydrotreated to remove impurities, sour water and sour gas streams will contain relatively low levels of hydrogen sulphide and ammonia in the fractionator.

Depending on the products desired and the size of the unit, hydrocracking is conducted in either single-stage or multistage reactor processes. Hydrocrackers can be classified into three categories: single-stage once-through; single-stage recycle and two-stage recycle. These categories are described below:

Only fresh feed is processed in the single-stage once-through hydrocracker. The conversions achieved are around 80 – 90 %, depending on the catalyst and reactor conditions. The heavy residue is either sent to the fuel oil pool or further processed in a catalytic cracker or coking unit.

In the single-stage recycle configuration, the unconverted oil is recycled to the reactor for further conversion, increasing the overall conversion to around 97 – 98 %. A small bleed stream of about 2 – 3 % on fresh feed is required to avoid a build-up of polyaromatics (PAH) in the recycle loop. Figure 2.20 shows a simplified process flow diagram of the single-stage hydrocracker with recycle configuration. In the first reactor beds, conversion of N and S compounds, saturation of olefins and partial saturation of PAH takes place. In the subsequent beds, the actual cracking will take place. The vapour from the low-pressure (LP) separator is used as refinery fuel after amine treating. Many different fractionation section configurations are found. A common fractionation section is illustrated in Figure 2.20. The product stream is fed to the debutaniser column to separate the LPG. The LPG stream is washed in an amine wash and then fractionated into a propane and a butane stream. The bottom stream from the debutaniser column is fed to the first fractionator. In this column, a light naphtha stream is taken as overhead product, heavy naphtha and kerosene are taken as side-streams and the bottom stream is fed to a second fractionator. In the second fractionator, operating at mild vacuum, the diesel product is taken as the overhead product and the bottom stream and the unconverted oil is recycled to the reactor section.

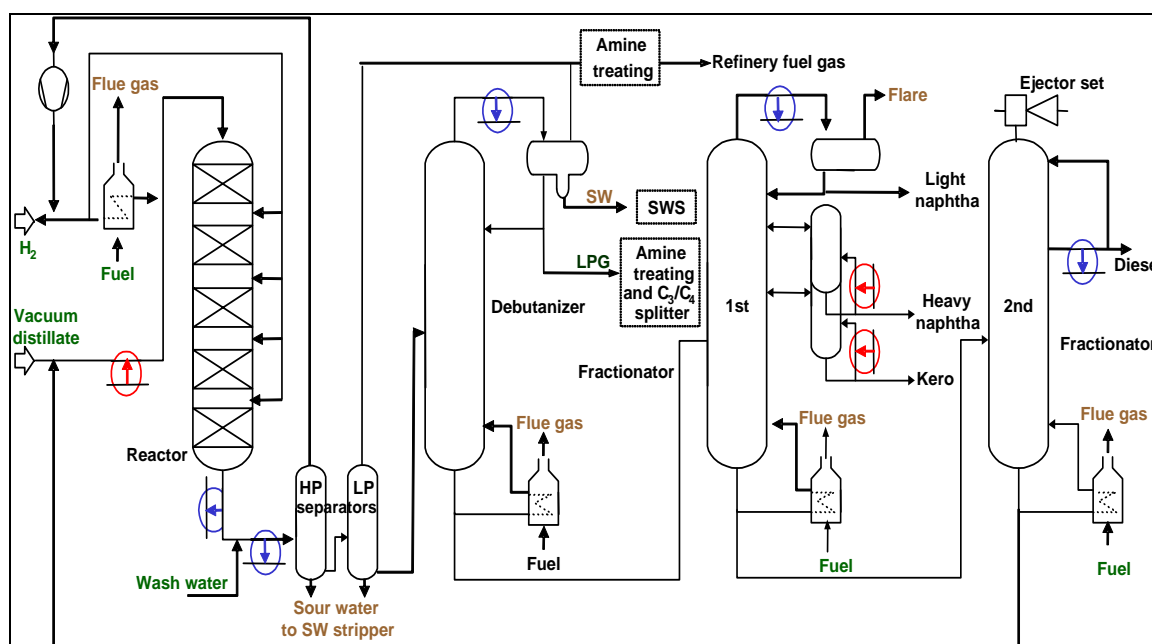


Figure 2.20: Simplified process flow scheme of a hydrocracker (single-stage with recycling)

In the two-stage recycle configuration, the first hydrocracker reactor operates in a once-through mode with a typical conversion of around 50 %. The unconverted oil from the first hydrocracker reactor is fed to a second hydrocracker reactor for further conversion. The unconverted oil from the second stage hydrocracker is recycled to achieve an overall conversion of around 97 – 98 %. A small bleed stream of about 2 – 3 % on fresh feed is also required here. This concept is normally applied when a very heavy high refractory feedstock such as deasphalted oil is processed. Two-stage configurations are usually more cost-effective for large capacity units, and more flexible and efficient for processing difficult feedstocks. By adjusting specific catalysts for each stage, most ammonia and hydrogen sulphide can be generated at the first stage, allowing a cleaner second stage reaction environment with improved middle distillate production yield and product quality. Table 2.9 shows the typical operating conditions of hydrocrackers

Table 2.9: Typical hydrocracker operating conditions

| Parameters | High-pressure hydrocracking | Moderate-pressure hydrocracking |
|---|-----------------------------|---------------------------------|
| Conversion, % w/w | 70 – 100 | 20 – 70 |
| Pressure, barg | 100 – 200 | 70 – 100 |
| Liquid hourly space velocity | 0.5 – 2.0 | 0.5 – 2.0 |
| Average reactor temperature °C | 340 – 425 | 340 – 425 |
| Hydrogen circulation, Nm ³ /m ³ | 650 – 1700 | 350 – 1200 |
| Source: [175, Meyers 1997] | | |

Hydroconversion

In principle, three reactions take place: hydrodemetallisation, hydrotreating/hydrogenation and hydrocracking. Removal of the metals from the residue feed predominantly occurs in the first reactor(s) and uses a low activity cobalt and molybdene (Co/Mo) catalyst. Hydrotreating, hydrogenation and hydrocracking occur in the following reactor(s) where the quality is mainly improved by increasing the hydrogen/carbon ratio. Conversion levels to products in a hydroconversion process are typically 50 – 70 %, but depend significantly on the type of hydroconversion process and the quality of the feedstock.

Figure 2.21 shows a simplified process flow diagram of a moving bed process. The process comprises five reactors in series, catalyst handling facilities and a work-up section. The reactors operate at high pressure and relatively high temperatures.

The first three reactors are bunker hydrodemetallisation (HDM) reactors. The nickel-vanadium (Ni+V) conversion typically exceeds 60 % for the first 60 days of operation and then gradually trends towards the expected equilibrium conversion level, 50 % to 70 %. This way, high-metal feeds can be treated.

The last two reactors are fixed bed desulphurisation and conversion reactors. The moving bed technology employs a bunker flow/moving bed technology to replenish the HDM catalyst continuously. Catalysts are transported through a slurry transport system in which the rate of catalyst replenishment is controlled in accordance with the rate of metal deposition. The catalyst in the HDM reactors flows concurrently downward with the process fluids. Screens separate the catalysts from the process fluids before leaving the reactor. Sluice systems are present at the top and the bottom of the reactors to enable catalyst addition and withdrawal.

The following conversion section consists of two fixed bed reactors in series, containing catalysts, that are highly active for sulphur removal and conversion. The ebullated bed reactor operates as a fluidised bed three-phase system with backmixing of the unconverted liquid and the catalyst.

The concept of the fractionation section is also very licensor-dependent as it depends on the configuration of the separator system and the resulting temperatures. Typically, it consists of a main fractionator, a vacuum distillation column, and some form of a gas plant to fractionate and stabilise the lighter fractions. Products from the fractionation section are normally refinery fuel gas, LPG, naphtha, kerosene, light gas oil, vacuum distillate and a low-sulphur/metal vacuum residue (bottoms) stream. The refinery fuel gas and LPG streams are amine washed to remove H₂S. The naphtha product is normally fed to a naphtha hydrotreater for further processing, identical to the straight-run naphtha product. The kerosene and light gas oil products are normally fed to a hydrotreater for further purification. The vacuum distillate is converted further in a hydrocracker or FCC unit. The bottom stream is normally blended into the heavy fuel oil pool or used as delayed coker feedstock.

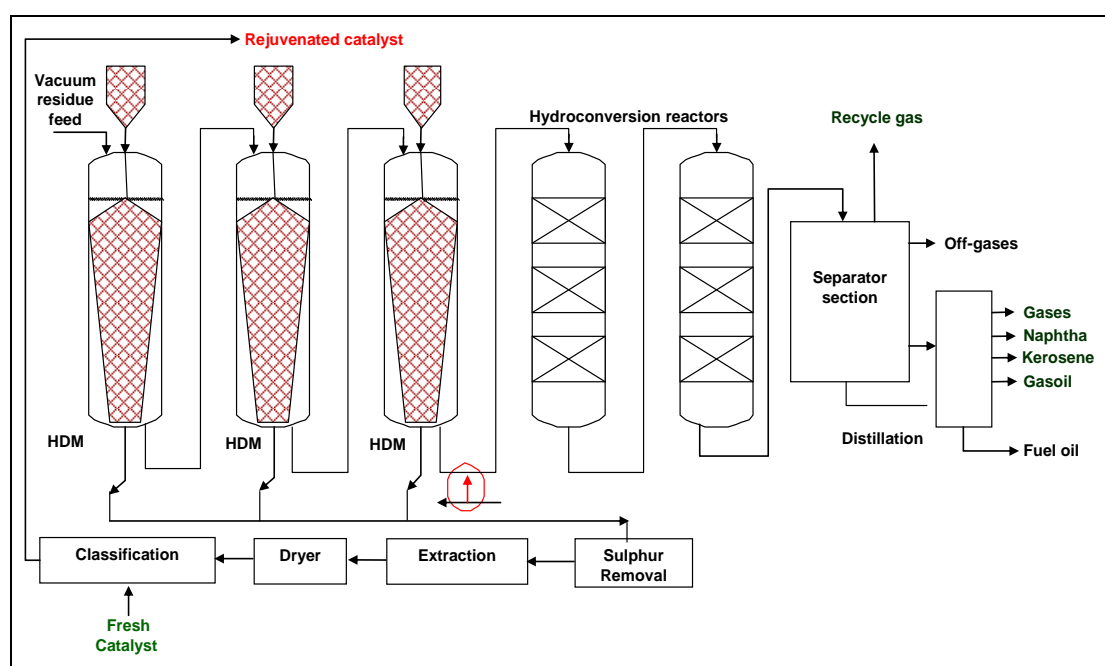


Figure 2.21: Simplified process flow scheme of a hydroconversion process (moving bed)

2.14 Hydrogen production

Purpose and principle

There is an increasing demand for hydrogen in European refining, due to an increased use of hydrocracking and hydrotreating. More hydrodesulphurisation is needed to achieve legislative requirements for lower sulphur content in fuels.

In such a context, the purpose of a hydrogen plant is to produce hydrogen for use in hydrocracking and other hydrogen-consuming refinery process units (Sections 2.13 and 2.16).

Hydrogen can be provided by one of the following processes:

- reforming operations (Section 2.6) for hydrotreating (refineries with the simplest configuration may produce sufficient quantities);
- steam reforming of light ends or natural gas;
- partial oxidation (gasification) of heavy oil fractions (IGCC in Section 2.10) to produce syngas where hydrogen can be separated.

Complex plants with extensive hydrotreating and/or hydrocracking operations typically require more hydrogen than is produced by their catalytic reforming units. The reliable operation of a hydrogen plant is critical for the hydrogen-consuming processes. Reactions that may occur in these processes are listed in Table 2.10.

Feed and product streams

The feed of the hydrogen plant consists of hydrocarbons in the range from natural gas to heavy residue oils and coke. The conventional steam reforming process produces a hydrogen product of a maximum of 97 – 98 % v/v purity and higher if a purification process is applied (99.9 – 99.999 % v/v). The partial oxidation process requires oxygen if oxygen-blown gasification is used instead of air-blown gasification.

Table 2.10: Main chemical reactions occurring in hydrogen production processes

| | |
|--|--|
| Steam reforming process | |
| $C_nH_m + n H_2O \rightleftharpoons n CO + (n+m/2) H_2$ | Generic for steam reforming (endothermic) |
| $CH_4 + H_2O \rightleftharpoons CO + 3 H_2$ | Steam methane reforming ($\Delta H = -206 \text{ kJ/mol}$ at 15 °C) |
| $CO + H_2O \rightleftharpoons CO_2 + H_2$ | Shift (exothermic) ($\Delta H = + 41.2 \text{ kJ/mol}$ at 15 °C) |
| $CO + 3 H_2 \rightleftharpoons CH_4 + H_2O$ $CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2O$ | Methanation (exothermic) |
| Partial oxidation | |
| $C_nH_m + n/2 O_2 \rightleftharpoons n CO + m/2 H_2$ | Generic for partial oxidation (endothermic) |
| $CO + H_2O \rightleftharpoons CO_2 + H_2$ | Shift (exothermic) ($\Delta H = + 41.2 \text{ kJ/mol}$ at 15 °C) |
| Gasification | |
| $C + H_2O \rightleftharpoons CO + H_2$ | Coke gasification ($\Delta H = -132 \text{ kJ/mol}$ at 15 °C) |
| $CO + H_2O \rightleftharpoons CO_2 + H_2$ | Shift (exothermic) ($\Delta H = + 41.2 \text{ kJ/mol}$ at 15 °C) |

In steam reforming, only light hydrocarbons are reacted with steam to form hydrogen. However, all products of a refinery could be used for hydrogen production by partial oxidation. The most interesting option from the economic point of view is to use products with a low market value. In some refineries, heavy oil residues are transformed to petroleum coke and subsequently gasified (Section 2.7) to produce syngas.

Hydrogen production strategy

Both reforming and gasification can lead to a reduced environmental impact at the overall site scale. The choice between these two approaches primarily depends on two factors:

- the availability and nature of excess hydrocarbon streams which may be used as feedstocks;
- the quantity of hydrogen required.

The primary advantage of a gasification strategy is that useful products are generated as raw synthesis gas containing carbon monoxide and hydrogen (see Table 2.11). It does so from heavier refinery hydrocarbon streams that would not otherwise have been used. Therefore, the implementation of gasification technology has an environmental and economic benefit on the overall refinery conversion performance. However, one clear limitation is that the hydrogen produced from gasification can only be considered a by-product. The heavier the feedstock, the lower the H_2/CO ratio: the most common solid and liquid refinery streams are going to yield a molar ratio less than 2 (see Figure 4.40 in Chapter 4.14.1). The economic and environmental viability of the gasification technology depends primarily on having a productive use of the resulting syngas/CO primary product. The second limitation arises from the availability of hydrogen within the refinery. More specifically, the heavier refinery hydrocarbon (waste) streams that would be gasified simply may not have enough hydrogen in them to produce the required quantity. In case of a very large hydrogen requirement (as is often the case), then an additional hydrogen supply (usually by light hydrocarbon steam reforming) would be needed.

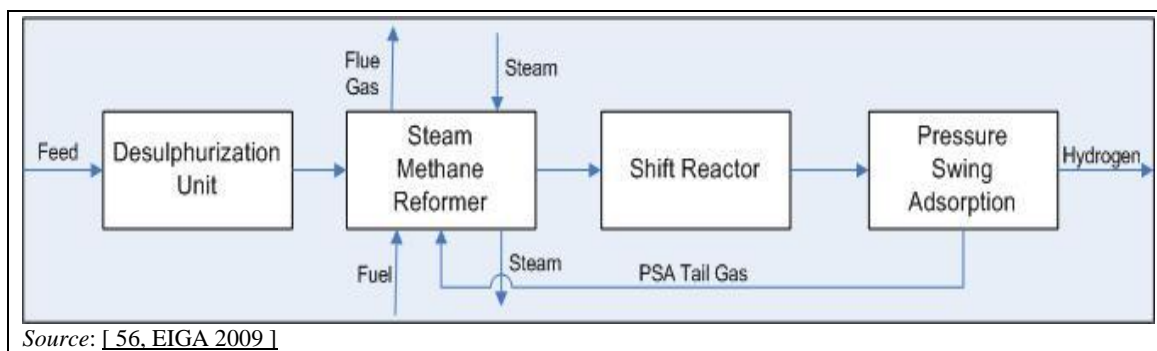
By using a steam reforming strategy, the yield is much higher. As such, hydrogen can be truly considered the primary product. However, the main limitation of this process is that it requires a light feedstock (natural gas, naphtha or other light hydrocarbon cuts), which is also a potential high value feedstock for other refinery or petrochemical applications, or a favourable fuel source for reducing the site PM, NO_x and SO_x emissions.

In all cases, hydrogen purification is necessary to meet the downstream desulphurisation process requirements. This is true for steam reforming, gasification, or any other already existing streams within the refinery.

Process description

Steam reforming

This is the most commonly used method for hydrogen production. The best feedstocks for steam reforming are light, saturated, and low in sulphur; this includes natural gas (the most common), refinery gas, LPG, and light naphtha. In its simplest form, as shown in Figure 2.22, the steam methane reforming process for pure hydrogen production consists of four stages: a desulphurisation unit, a steam methane reformer, shift reactor(s), and finally pressure swing adsorption.



Source: [56, EIGA 2009]

Figure 2.22: The four main steps of H₂ production by steam methane reforming

The reaction is typically carried out at 750 – 1000°C and a pressure of 20 – 40 barg over a fixed catalyst bed, which is very sensitive to poisoning. Desulphurisation of the feedstock is required in order to protect the catalyst in the reformer furnace against deactivation.

It is common practice to operate at excess steam/hydrocarbon ratios to prevent carbon formation. Heat for the endothermic reforming reaction is provided by the furnace burners. The reformed gas, a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and steam, is cooled down to about 350 °C by rising steam. After reforming, the CO in the gas is reacted with steam to form additional hydrogen (shift reaction).

The oxidation of the CO to CO₂ can be done in a one-step (low, medium or high temperature) converter in a two-step shift (high followed by low temperature) converter, reducing the CO content to less than 0.4 %. The product gas passes to a PSA which delivers ultra-pure hydrogen. The PSA tail gas is recycled to the steam-methane reformer burners as shown in Figure 2.22.

More information on hydrogen production can be found in the LVIC-AAF BREF [92, COM 2007].

Gasification of coke

The processes used for the gasification of petroleum coke are the same as those used in the gasification of coal and they are integrated in the Flexicoker (See Section 2.7). In an oxygen-blown operating mode of a gasifier, the gas produced can be processed to recover hydrogen or synthesis gas, or can be used as a medium-calorific value fuel. The gasifier product gas (syngas, CO, H₂, CO₂, CH₄ and H₂O), after it has passed the cyclones, contains hydrogen sulphide (H₂S) and carbonyl sulphide (COS). With a sulphur adsorbent such as limestone (CaCO₃) or dolomite (Mg, CaCO₃) in the gasifier, the sulphur content of the gas can be drastically reduced. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. The particulates in product gas are removed in the barrier filter. Volatile metals and alkali tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burnt and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas.

Table 2.11: Example of composition of petroleum coke used and the composition of the syngas produced in an oxygen-blown fluidised bed gasification process

| Analysis of petroleum coke used in gasification | | Composition of gas produced by gasification at 980 – 1135 °C | |
|---|-------------|--|-------------|
| Ultimate analysis | % w/w | | % v/v |
| Carbon | 87.1 – 90.3 | CO | 34.3 – 45.6 |
| Hydrogen | 3.8 – 4.0 | CO ₂ | 27.3 – 36.4 |
| Sulphur | 2.1 – 2.3 | Hydrogen | 13.5 – 16.8 |
| Nitrogen | 1.6 – 2.5 | Water | 8.7 – 13.9 |
| Oxygen | 1.5 – 2.0 | Methane | 0.1 – 0.9 |
| Proximate analysis | | Nitrogen | 0.4 – 0.7 |
| Fixed carbon | 80.4 – 89.2 | H ₂ S | 0.3 – 0.6 |
| Volatiles | 9.0 – 9.7 | | |
| Moisture | 0.9 – 10.2 | | |
| Ash | 0.2 – 0.4 | | |

Source: [175, Meyers 1997]

Gasification of hydrocarbons (partial oxidation)

In partial oxidation, hydrocarbon feed reacts with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide (also covered in IGCC in Section 2.10). Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the light, clean feedstocks required for steam reforming.

Hydrogen processing in this system depends on how much of the gas is to be recovered as hydrogen, and how much is to be used as fuel. Where hydrogen production is a relatively small part of the total gas stream, a membrane is normally used to withdraw a hydrogen-rich stream. That stream is then refined in a purification unit.

Purification of hydrogen

A wide variety of processes are used to purify hydrogen streams. Since the streams are available at a wide variety of compositions, flows, and pressures, the method of purification will vary. They include wet scrubbing, membrane systems, cryogenic separation and pressure swing adsorption (PSA). This last technique is the most commonly used. In the PSA plant, most impurities can be removed to any desired level. Several layers of adsorbents (molecular sieves) remove carbon dioxide, water, carbon monoxide, methane and nitrogen from the out-stream. Nitrogen is the most difficult to remove of the common impurities, and removing it completely requires additional adsorbent. Since nitrogen acts mainly as a diluent, it is usually left in the product if the hydrogen is not going to be used in a very high-pressure system such as a hydrocracker or a common network. Hydrogen purity is 99.9 – 99.999 % v/v after the PSA unit. The residual constituent of the product gas is usually less than 10 ppm CO. Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is used as fuel at a convenient location.

2.15 Integrated refinery management

All refinery process units, systems and activities are typically operated in an integrated way, aimed at optimising production in a way that is economic, sustainable and acceptable to society. This requires a concerted well-managed approach in the execution and planning of all activities likely to impact on the site environmental performance.

Sections 15 of Chapters 2, 3 and 4 aim at describing general management activities related to the environment, with a focus on several aspects of housekeeping, soil and groundwater protection, and utility management which are particularly relevant to the refining sector. These Sections have been structured according to the two following categories.

- Refinery management activities including environmental management tools and good housekeeping techniques. Within this section, activities such as maintenance, cleaning, good design, production planning (including start-ups and shutdowns), training, information system process supervision/control systems and safety systems have been included.
- Utilities management within a refinery not covered by other sections, such as water management, blowdown systems, compressed air generation and distribution and electricity distribution systems.

Refinery management activities

Environmental management tools

An environmental management system (EMS) is a system for managing all activities (including energy) in a refinery that presents the purpose of the refinery as a whole, the responsibilities of employees/management and procedures to be followed. An intrinsic aim of EMS is to achieve continuous improvement, with a refinery learning, in particular, from its own operational experience, as well as that of others. See also Section 4.15.1.1 on EMS.

The development of EMS started by building upon the experience gained by other business parameters. Quite often, management responsibility for the environment is placed on the same person with the management responsibility for safety, health, and sometimes quality. Environmental management is also named environmental care. In this section the importance of good housekeeping and management is highlighted. It is remarked that systems exist for improving performance in many fields, such as safety, maintenance and product quality. Environmental Management Systems have also been developed for the improvement of refinery performance in environmental matters.

Good housekeeping

Good housekeeping techniques refer to the proper handling of the day-to-day aspects of running a refinery. Many daily refinery activities undertaken in various domains like maintenance, cleaning, new process and process modification development, production planning (including start-ups, shutdowns), information systems process supervision/control, and training and safety are likely to have an impact on environmental performance and should be managed properly in that respect. Other European regulatory schemes, like the Council Directive 96/82/EC on the control of major-accident hazards, underline the importance of proper housekeeping and the obligation to plan and control activities efficiently within the refinery EMS.

Heat exchanger cleaning

Heat exchangers are widely used throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream. The bundles are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Therefore, heat exchanger cleaning is one issue of particular importance to be addressed within refinery management activities.

Utilities management

Energy management including steam management and cooling are included in other Sections 8 and 10.

Water management

Water is used within a refinery as process water, boiler feed, firefighting preparedness and cooling water and these require adequate management before discharge into the receiving environment. Besides these, any precipitation like rainwater (clean or contaminated) is another type of water that should also be considered. In addition, sanitary waste water, ballast water and blowdown water are other sources of waste water that may require treatment before discharge.

Water master plans are normally applied to refineries in order to optimise the consumption of water. Water inventories are sometimes a great help in the management of water, matching the quantity and quality of the effluents. Water integration and management is dependent on the refinery configuration, the crude quality and the level of desalting required, the cost of potable water, the availability of rainwater and the quality of the cooling water.

Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available, as well as a number of standard possibilities for water reduction and reuse. In most refineries, a number of these options have already been implemented to some extent, either in the original design or by retrofit. Segregation of process water discharges and other types of water are also points to consider in the water management system. Ballast water is relevant to these refineries that have crude receipt facilities from ships or handle big product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and contaminated with oil and will require appropriate treatment. However, volumes of ballast water to be treated are declining with the gradual introduction of segregated ballast tankers.

Water drainage applies to any industrial site. It entails the complete system of fresh water supply, rainwater, ballast water, process water, cooling water and groundwater, as well as effluent collection, storage and the various waste water treatment systems. The design is based on local factors (rainfall, receiving water bodies, etc.), effluent segregation, source reduction, first flush approach, flexible routing and reuse options.

Recirculated process water streams and cooling water streams are often manually purged to prevent the continued build-up of contaminants in the stream (blowdown system).

Purge/vent systems

Most refinery process units and equipment are arranged into a collection unit, called the purge/vent system. These systems provide for the safe handling and disposal of liquid and gases, as well as for shutdown, cleaning and emergency situations. Purge/vent systems are either automatically vented from the process units through pressure relief valves, or are manually drawn from units. Part or all of the contents of equipment can also be purged prior to shutdown before normal or emergency shutdowns. Purge/vent systems use a series of flash drums and condensers to separate the blowdown into its vapour and liquid components.

Compressed air generation

Compressed air is necessary as a utility within a refinery. It is normally generated by electric compressors and is distributed around the refinery.

Heating of pipes

Current practices are to apply steam heating (low-pressure steam), electric heating or hot oil heating of lines, if it is required. Electric heating normally generates less corrosion and consequently is easier to maintain compared with heating using steam. Hot oil heating is used when high temperatures are needed.

2.16 Isomerisation

Purpose and principle

Isomerisation is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, low-molecular-weight paraffins (C_4 - C_6) are converted to isoparaffins with a much higher octane index. The isomerisation of olefins is also included in this section.

Feed and product streams

Typical feedstocks to isomerisation units are any butane-, pentane- or hexane-rich feed stream. These streams are hydrotreated naphtha, straight run light naphtha, light naphtha from hydrocrackers, light reformate, coker light naphtha and the light raffinate stream from an aromatic extraction unit. The feed stream to a C_5/C_6 isomerisation unit is normally fractionated so that it includes as much of the C_5/C_6 as possible, while minimising heptanes and heavier compounds.

Process description

Figure 2.23 shows a simplified process flow diagram of a low-temperature isomerisation unit with hydrogen and hydrocarbon recycle. The isomerisation reactions occur in the presence of hydrogen and catalyst. The atmosphere of hydrogen is used to minimise carbon deposits on the catalyst, but with a low hydrogen consumption. The reactions normally take place in two reactors in a series. An advantage of the two-reactor scheme is that the first reactor may operate at higher temperatures to kinetically drive the reactions, while the tail reactor may be operated at lower temperatures to push the desired products closer to equilibrium conversion.

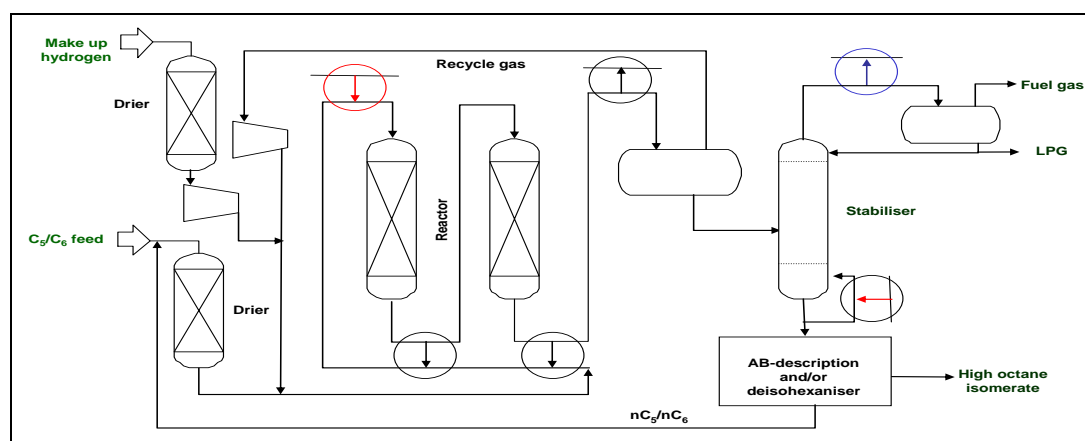


Figure 2.23: Simplified process flow scheme of an isomerisation unit

There are several isomerisation process designs based on three isomerisation catalyst technologies that can be further designed to operate with or without hydrogen recycle and with or without hydrocarbon recycle. In general, they can be classified into two categories, 'hydrocarbon once-through' or 'hydrocarbon recycled'.

- In 'once-through' isomerisation designs, only fresh feed is processed in the isomerisation unit. The octane number which can be achieved is only around 77 – 80 RON when using a zeolite-based catalyst, and 82 – 85 RON using a chloride-promoted catalyst. Conversions of 80 % can be expected.
- In hydrocarbon recycle isomerisation designs, the unconverted, lower octane paraffins are recycled for further conversion. Depending on the recycle option, the recycle may be normal paraffins or methylhexanes and n-hexane. The octane number obtained can be up to 92 RON, dependent on the feedstock composition, configuration and catalyst used. The

yield in the isomerate is around 95 – 98 %, depending on the targeted octane number of the final stream.

There are three distinctly different types of isomerisation catalysts currently in use:

- chloride-promoted
- zeolitic
- sulphated-zirconia catalysts.

The zeolite catalyst operates at significantly higher temperatures (250 – 280 °C and 15 – 25 barg) and is more tolerant to contaminants, though the resulting octane improvements are lower. The zeolite catalyst is mainly used when higher octane isomerate product does not justify the additional capital required to reduce feed contaminants for the chloride-alumina catalyst or is a better match for a retrofit unit. The highly active chloride-promoted catalyst operates at a relatively low temperature (130 – 180 °C and 30 barg) and gives the highest octane improvement. This type of catalyst requires the addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor to maintain the high activity. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. Furthermore, this catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to less than 0.5 ppm is required. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to the desired isomers is enhanced at lower temperatures.

After isomerisation, the light ends are fractionated from the product stream leaving the reactor and are then sent to refinery fuel gas or to the light ends recovery unit. In a hydrocarbon once-through isomerisation unit, the bottom stream from the stabiliser is, after product cooling, sent to the gasoline pool. In a hydrocarbon recycle isomerisation design, the bottom stream from the stabiliser is fed to a separation unit, which is either a deisohexaniser column or an adsorption system.

In the deisohexaniser column, a split can be made between the higher octane dimethylbutanes and the lower octane methylpentanes. The dimethylbutanes and lower boiling C₅ components (isomerate product) are taken overhead from the column and are sent to the gasoline pool. The methylpentanes and normal hexane are taken as a side-stream close to the bottom, and are recycled to the isomerisation reactor. The bottom stream from the deisohexaniser is a small quantity of heavy by-product which is sent with the isomerate product to the gasoline pool or to a catalytic reformer if the refinery recovers benzene as chemical feed. The principle of adsorption is that the unconverted normal paraffins are adsorbed on the molecular sieve whereas the isoparaffins pass the adsorbent. Desorption takes place with heated hydrogen-rich gas from the separator or a butane mixture. The desorbent is separated from the net hydrogen-rich recycle stream in a separator vessel and returned to the isomerisation reactor for further conversion.

2.17 Natural gas plants

Natural gas refined in Europe has been largely up to this point in time from the North Sea basin. Natural gas is also obtained from a small number of onshore oilfields, where it is co-produced with crude oil and separated at local facilities before being treated, brought up to specification and finally exported. Offshore gas production consists of a number of central platforms with satellite platforms and is sent via pipeline systems to coastal refining terminals. However, offshore platforms are not included in the scope of this document.

Descriptions

The following processes are generally in place at a gas refinery:

- gas Dewpointing;
- inlet Reception Facilities;
- glycol Recovery, Reuse and storage;
- gas Heating and Pressure Reduction;
- H₂S Removal;
- gas Metering and Export;
- condensate Separation and Stabilisation;
- condensate Storage, Metering and Export;
- propane Refrigeration System.

The extent to which the initial gas refining is completed offshore is dependent on the type of facility available and the nature of the gas from the wells. At some well-head facilities the process involves the removal of all condensate and water, which are removed to shore via other routes. For the rest of the gas streams the condensate fraction is removed and then re-injected back into the system. It is also at this stage that glycol (commonly mono-ethylene glycol) is injected for the purpose of anti-freeze. The gas stream may also have scale inhibitors added at this stage to prevent hydrate formation within the pipelines.

Gas reception facilities usually include sphere pig receivers and slug catchers. The slug catchers are large volume low-pressure sections of pipeline, which are there to knock down the water and dust entrained with the gas.

Gas Dewpointing is part of the true refining section of the process. The gas is cooled usually using propane heat exchangers (the propane will freeze during this process and is subsequently recycled through re-boilers). It is through this process that the final gas stream quality is achieved, in combination with a final metering and mixing stage to achieve sales gas quality.

H₂S Removal: The majority of the gas wells in the North Sea are sweet and the number of sour wells has fallen over the past few years, but most terminals will have the ability to deal with feedstocks which have small percentages of sour gas. The main principles used are amine gas treatment or catalysed bed system.

Condensate Separation and Stabilisation: The usual method is to remove the lighter fractions in the refining process and some of the more volatile elements. Condensate is then either refined on site or shipped to a refining site, which will produce kerosene and naphtha for sale as an important economic by-product.

Glycol system: This is a recirculation system, with the glycol being pumped offshore injected into the feed gas stream, and then removed early in the process. It is re-boiled and cleaned up via filters and prepared to be re-injected into the system.

Purpose and principle

The overall objective of natural gas processing is to remove the treatment chemicals and to remove any contaminants from the well-head stream, in order to produce a methane-rich gas

which satisfies statutory and contractual specifications. The main contaminants to be removed fall into the following categories:

- solids: sands, clay, sometimes scale like carbonates and sulphates (including naturally occurring radioactive metals (e.g. lead or radium), mercury);
- liquids: water/brine, hydrocarbons, chemicals added at the well head;
- gases: acid gases, carbon dioxide, hydrogen sulphide, nitrogen, mercury and other gases (e.g. mercaptans).

Feed and product streams

The feedstock is natural gas and the products that may be separated within the natural gas plants are methane-rich gas, C₂, C₃, C₄ fractions and condensates (C₅₊).

Process description

As shown in Figure 2.25, the purification plant consists of an acid gas treatment (sweetening plant) where acid gases such as CO₂, H₂S, SO₂ are separated. Natural gas is considered ‘sour’ when it contains significantly greater amounts of hydrogen sulphide than those required to comply with the pipeline quality specifications or when it contains such amounts of SO₂ or CO₂ to make it impractical to use without purification. The H₂S must be removed (called ‘sweetening’ the gas) before the gas can be utilised. If H₂S is present, the gas is usually sweetened by absorption of the H₂S in an amine solution. Amine processes are the most common process used in the United States and Europe.

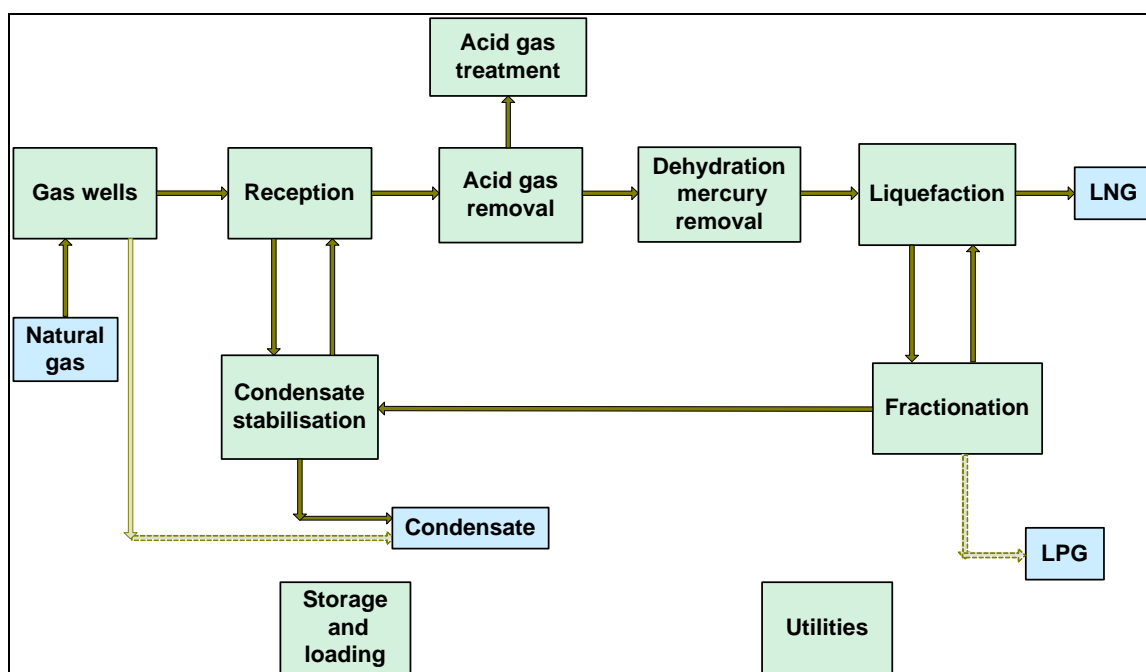


Figure 2.24: General block diagram of a natural gas plant

Other methods, such as carbonate processes, solid bed absorbents, and physical absorption, are employed in other sweetening plants.

Natural gasoline, butane and propane are usually present in the gas, and gas processing plants are required to recover these liquefiable constituents (see Figure 2.25). The type of processes found are very similar to those described in Section 2.12. As a summary, these processes are physical separations at very low temperatures (typically distillation). The following figures describe two of the main steps of the natural gas separation process.

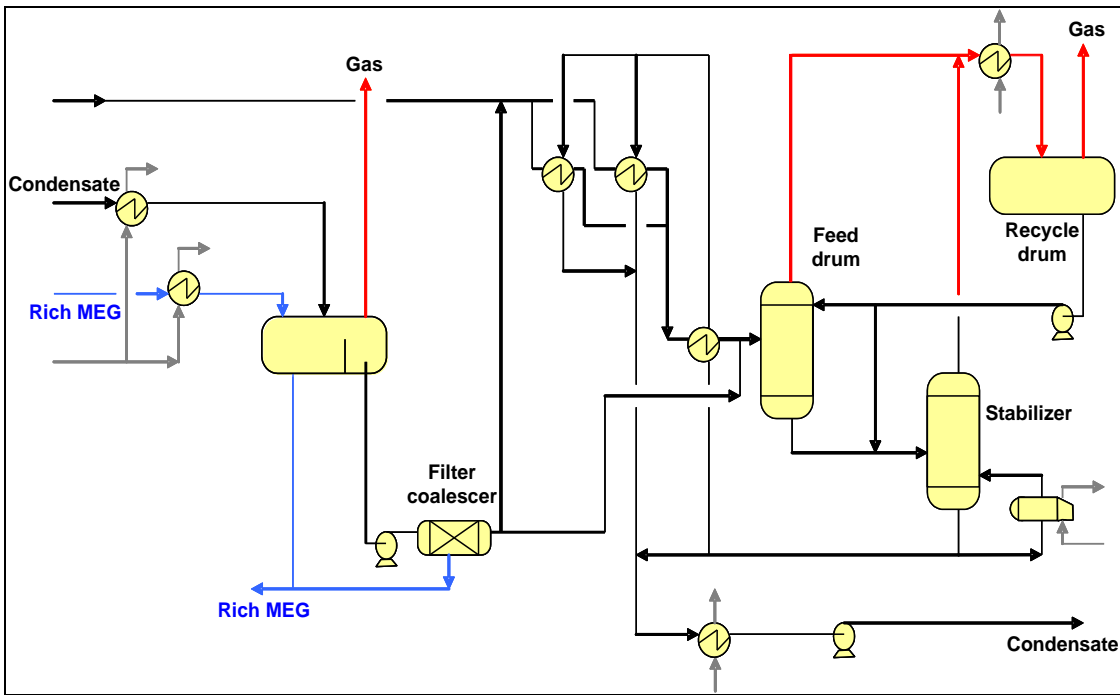


Figure 2.25: Condensate separation in a natural gas plant

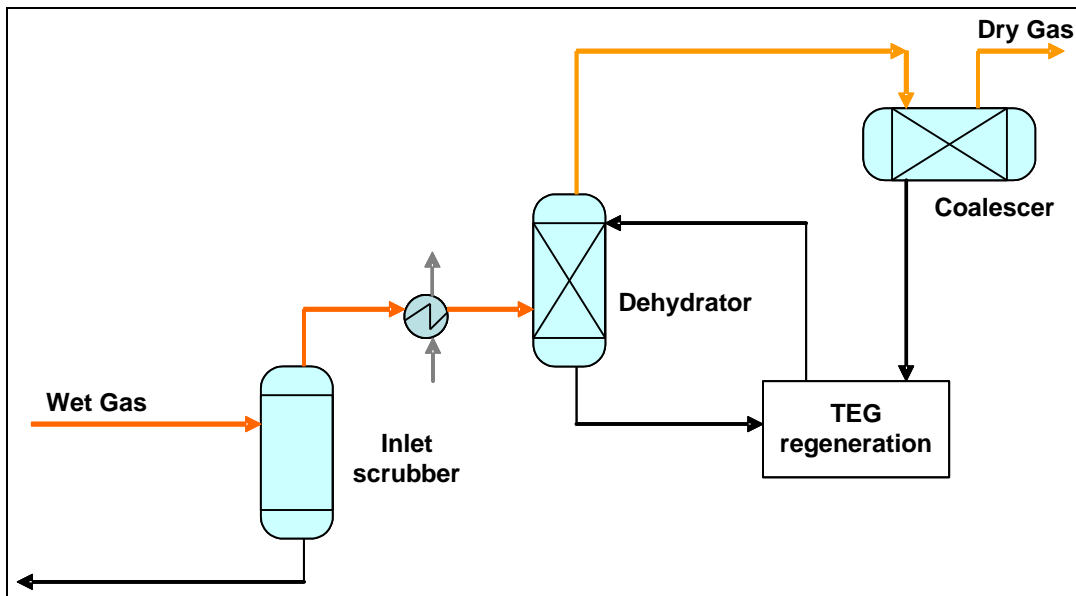


Figure 2.26: Gas dehydration in a natural gas plant

2.18 Polymerisation

This section covers the polymerisation, dimerisation and condensation of olefins.

Purpose and principle

Polymerisation is occasionally used to convert propene and butene to high-octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. Prevailing chemical reactions may vary according to olefin type and concentration but can be described in the general terms shown below.

| | | | |
|---|---------------|---------------------------|------------------|
| $2 \text{ C}_3\text{H}_6$ | \rightarrow | C_6H_{12} | (dimerisation) |
| $2 \text{ C}_4\text{H}_8$ | \rightarrow | C_8H_{16} | (dimerisation) |
| $\text{C}_3\text{H}_6 + \text{C}_4\text{H}_8$ | \rightarrow | C_7H_{14} | (condensation) |
| $3 \text{ C}_3\text{H}_6$ | \rightarrow | C_9H_{18} | (polymerisation) |

Feed and product streams

Propene and butene contained in the LPG stream from the FCC are the most common feed streams for this unit.

Process description

The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst adsorbed onto natural silica and extruded in pellets or in small cylinder forms. All reactions are exothermic, and therefore the process requires temperature control. The feed must be free of: sulphur, which poisons the catalyst; basic materials, which neutralise the catalyst and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans, then with an amine solution to remove hydrogen sulphide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer. A simplified scheme of a polymerisation unit is shown in Figure 2.27.

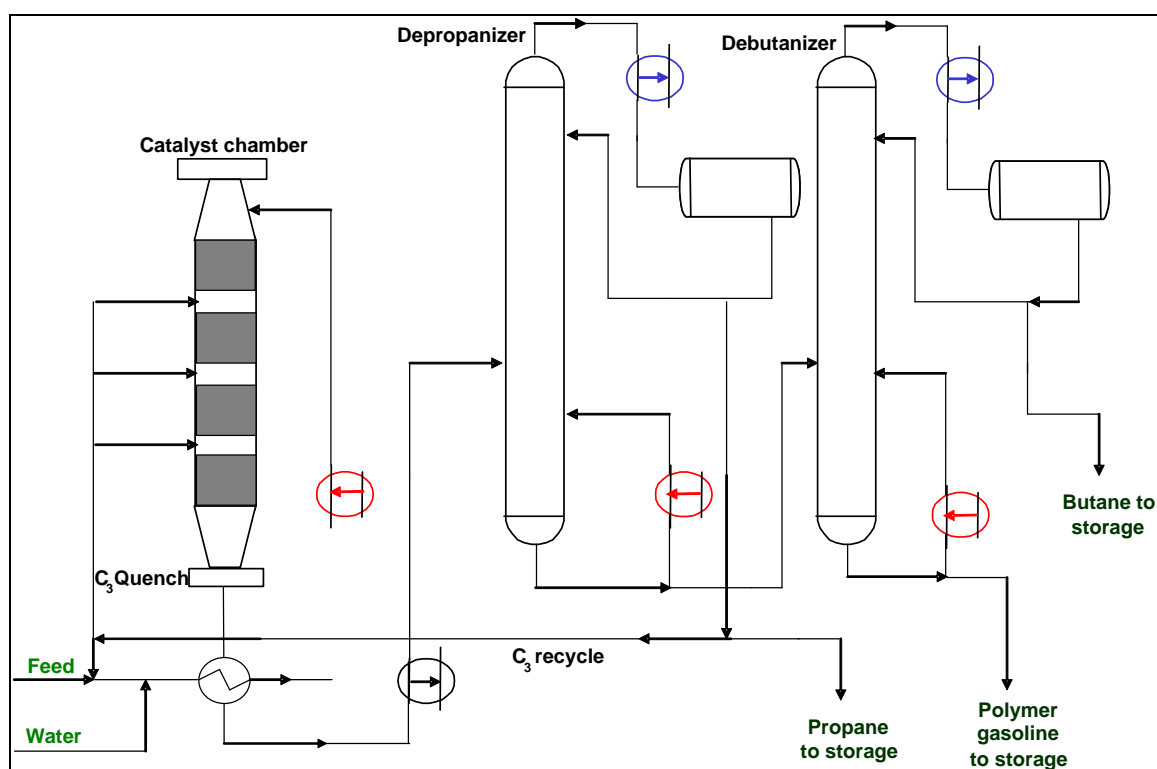


Figure 2.27: Simplified scheme of a polymerisation unit

When the polymerisation yield drops, the catalysts need to be replaced. After nitrogen purging, the polymerisation unit is opened and the catalyst removed by means of a high-pressure water jet. It can also be removed using steam (compression dumping). The phosphoric acid goes in the water medium, while the natural silica pellets break down to form a slurry, which is usually pumpable.

2.19 Primary distillation units

This section includes atmospheric and vacuum distillation. These two primary distillations are preceded by crude oil desalting and they are the first and fundamental separation processes in a refinery.

Purpose and principle

The Atmospheric Crude Oil Distillation Unit (CDU) is the first important processing step in a refinery. Crude oil is heated to elevated temperatures and then generally subjected to distillation under atmospheric pressure (or slightly higher), separating the various fractions according to their boiling range. Heavier fractions from the bottom of the CDU, which do not vaporise in this column, can be further separated later by vacuum distillation.

Increased demand for light products and a reduced demand for heavy fuel oil have resulted in refiners upgrading the atmospheric residue into more valuable lower boiling fractions such as naphtha, kerosene and mid-distillates. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure to increase volatilisation and separation whilst avoiding thermal cracking. The high vacuum unit (HVU) is normally the first processing step in upgrading atmospheric residue, followed by downstream refining units. The HVU produces feedstocks for cracking units, coking, bitumen and base oil units. The contaminants from the crude oil stay predominantly in the vacuum residue.

Feed and product streams

The crude oil feed to the crude distillation unit is supplied from the crude oil storage tanks after desalting. Normally all crude oil entering a refinery passes through a crude distillation unit. In addition, it is common practice that off-specification product streams are reprocessed in the CDU. The products from the crude distillation unit, ranging from the lightest to the heaviest cut are: naphtha and light components (boiling $<180\text{ }^{\circ}\text{C}/\text{C}_1\text{-C}_{12}$ - lights, naphtha and gasoline), kerosene (boiling range $180 - 240\text{ }^{\circ}\text{C}/\text{C}_8\text{-C}_{17}$), light gas oil (boiling range approximately $240 - 300\text{ }^{\circ}\text{C}/\text{C}_8\text{-C}_{25}$), heavy gas oil (boiling range approximately $300 - 360\text{ }^{\circ}\text{C}/\text{C}_{20} - \text{C}_{25}$) and atmospheric residue (boiling $>360\text{ }^{\circ}\text{C}/>\text{C}_{22}$). The overhead of this column is the light fraction, non-condensable refinery fuel gas (mainly methane and ethane). Typically, this gas also contains hydrogen sulphide and ammonia gases. The mixture of these gases is known as 'sour gas' or 'acid gas'. A certain amount of it passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide.

The main feed stream to the HVU is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue. In addition, the bleed stream from the hydrocracker unit (if applicable) is normally sent to the HVU for further processing. The products from the HVU are light vacuum gas oil, heavy vacuum gas oil, and vacuum residue. Light vacuum gas oil is normally routed to the gas oil hydrotreater(s), heavy gas oil is normally routed to a fluid catalytic cracker and/or hydrocracker unit. The vacuum residue can have many destinations, such as visbreaking, flexicoking or delayed coking, residue hydroprocessing, residue gasification, bitumen blowing or it may go to the heavy fuel oil pool.

Process description

Atmospheric distillation

Distillation involves the heating, vaporisation, fractionation, condensation, and cooling of feedstocks. The desalted crude oil is heated to about $300 - 400\text{ }^{\circ}\text{C}$ and fed to a vertical distillation column at atmospheric pressure, where most of the feed is vaporised and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected towards the top of the column.

The overhead hydrocarbon vapours are condensed and accumulated in the overhead reflux drum of the main fractionator. In this drum, sour water, light fractions (about 0.5 % on crude charge) and stripping steam (1.5 % on crude) are separated from the hydrocarbon liquid. The overhead hydrocarbon liquid, the naphtha minus stream, is commonly fed directly to the downstream naphtha treater.

Within each atmospheric distillation tower, a number of side-streams of low-boiling point components are removed from different trays in the tower. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side-streams are each sent to a different small stripping tower, containing four to ten trays with steam injection under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light ends are fed back to the atmospheric distillation tower above the corresponding side-stream draw tray.

Most of these fractions generated in the atmospheric distillation column can be sold as finished products after a hydrotreatment, or blended with products from downstream processes. In Figure 2.28, a simplified process flow diagram of a crude distillation unit is shown. Many refineries have more than one atmospheric distillation unit.

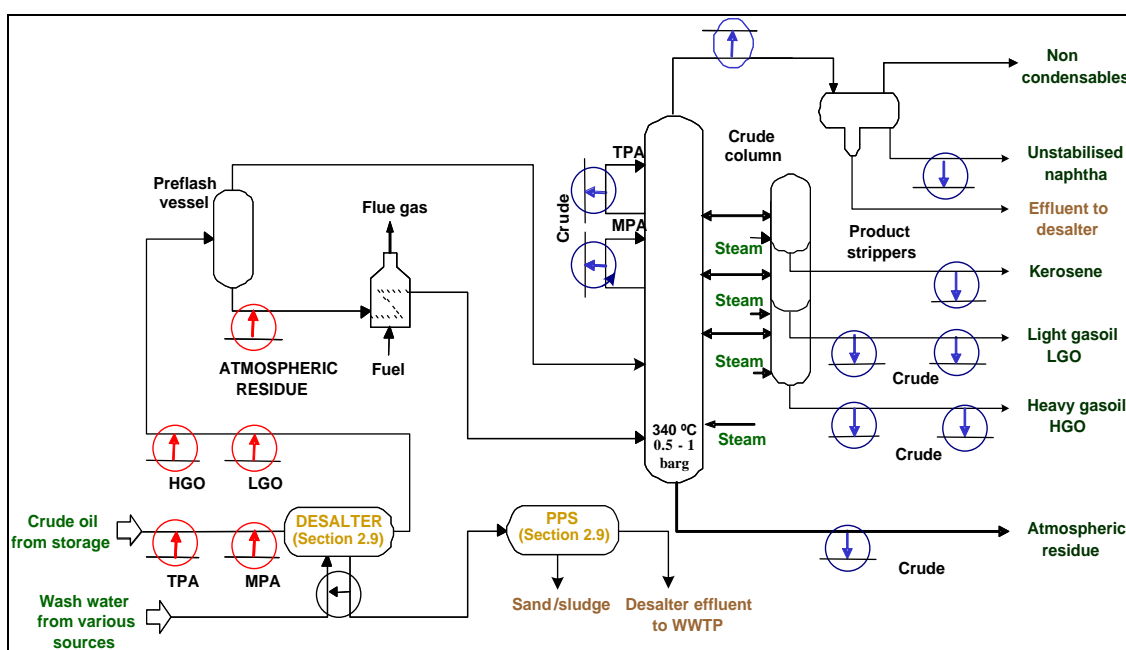


Figure 2.28: Simplified process flow diagram of a crude distillation unit

The operating conditions of the tower are based on the properties of the crude oil and the desired product yields and quality. To maximise the yield of distillates, the pressure is minimised, but the temperature is increased to the maximum. Every refinery has a crude distillation unit designed for a selected crude (mix). There are therefore many different crude distillation configurations with varying product cuts and heat integration.

Vacuum distillation

Figure 2.29 shows a simplified process flow diagram of the high vacuum unit. Atmospheric residue is heated up to 400 °C, partially vaporised (30 – 70 % w/w), and flashed into the base of the vacuum column at a pressure between 40 and 100 mbar (0.04 – 0.1 kg/cm²). The vacuum inside the fractionator is maintained with steam ejectors, vacuum pumps, barometric condensers or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporisation and separation.

The unvaporised part of the feed forms the bottom product and its temperature is controlled at about 355 °C to minimise coking. The flashed vapour rising through the column is contacted with wash oil (vacuum distillate) to wash out entrained liquid, coke and metals. The washed vapour is condensed in two or three main spray sections. In the lower sections of the column, the heavy vacuum distillate and optional medium vacuum gas oil are condensed.

In the upper section of the vacuum column, the light vacuum distillate is condensed. Light (non-condensable) components and steam from the top of the column are condensed and accumulated in an overhead drum for separating the light non-condensables, the heavier condensed gas oil, and the water phase.

The most important operational aspect of a vacuum unit is the quality of the heavy vacuum gas oil, especially when this is fed to a hydrocracker unit. The Concarbon level and/or metal content is critical for a hydrocracker unit and depends on the operation and performance of the wash oil section in the vacuum distillation unit, as well as the desalter in the crude distillation unit.

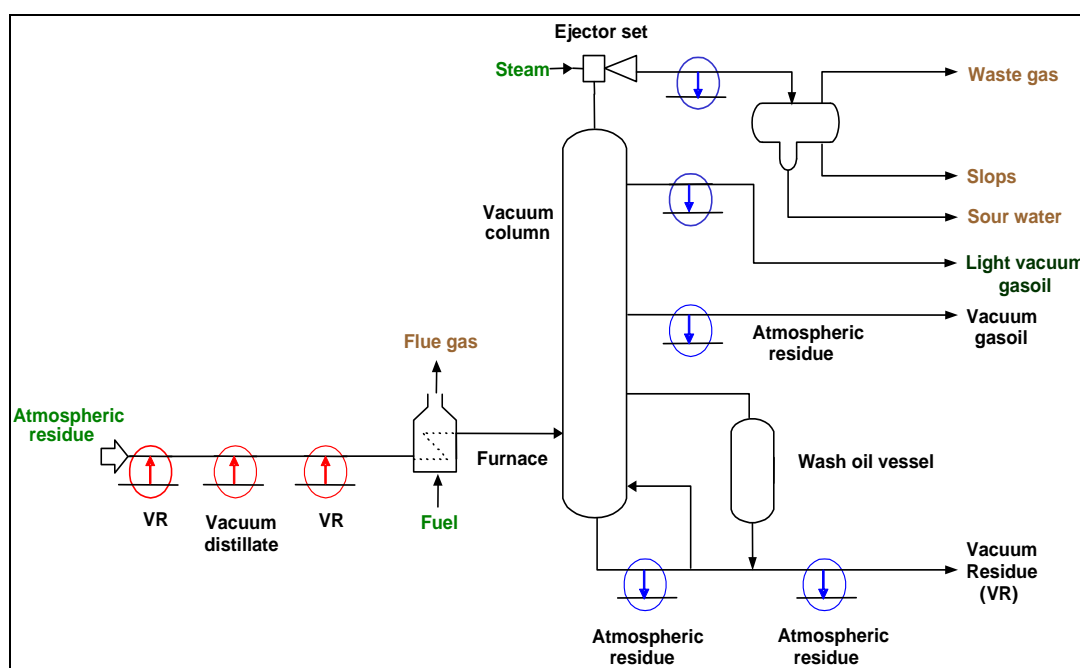


Figure 2.29: Simplified process flow scheme of a high vacuum distillation unit

2.20 Product treatments

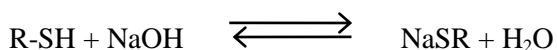
The treatments used in a refinery to achieve certain product specifications are included in this section, in which two types of processes can be identified.

- The first group of processes corresponds to extraction or removal techniques where the component to treat is removed from the stream to be treated. Under this category, mention can be made of molecular sieve extraction for the removal of carbon dioxide, water, hydrogen sulphide or mercaptans (Section 4.23.5.3), amine scrubbing for the removal of hydrogen sulphide (included in Section 4.23.5.1), and caustic washing for the removal of acids or mercaptans.
- The second group is composed of these systems where the chemical to be treated is not removed from the stream to be treated, e.g. by catalytic dewaxing process.

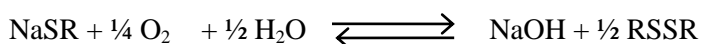
Extraction processes

Purpose and principle

In petroleum refining, chemical treatment is used to remove or change the undesirable properties associated with sulphur, nitrogen, or oxygen compound contaminants contained in petroleum products. Some of these systems (i.e. 'mercaptan oxidation') are designed to reduce the mercaptan content (organic sulphur compounds) of hydrocarbon streams to improve product odour and to reduce corrosivity. These treatments are accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. The extraction process removes the mercaptans by caustic extraction, resulting in a lower sulphur content. The following reaction takes place at low temperatures:



Mercaptan oxidation-sweetening is another version of the mercaptan oxidation process in which the mercaptans in the hydrocarbon products are converted to less odorous and less corrosive disulphides which remain in the product. The reaction is:



As a result no reduction in the total sulphur content takes place during sweetening and, consequently, it is only applied to these streams where the sulphur content is not a problem.

Feed and product streams

The mercaptan oxidation-extraction process entails the removal of mercaptans from LPG, naphtha, gasoline and kerosene streams. Oxidation or 'sweetening' is used on gasoline and distillate fractions. It should be stressed that mercaptans are also removed by hydrotreatment (Section 2.13).

Process description

Mercaptans are removed from light hydrocarbon streams by a concentrated alkaline wash in an extraction column under elevated pressure (5 barg). If H₂S or acids are present, a caustic prewash is required. The treated and odour-free hydrocarbon stream leaves the reactor as an overhead stream.

The aqueous bottom phase is heated to 50 °C, mixed with air, and fed to the oxidation reactor. The dissolved NaSR is now converted into disulphides (which are insoluble in caustic soda water solution) at 4.5 barg. By using an excess of air and adding catalyst, a high rate of reaction is maintained. In this way, the alkaline solution is regenerated. The liquid from the reactor is routed to a vessel where spent air, the disulphide fraction insoluble in the caustic solution and the caustic solution are separated. The spent air is routed to an incinerator or process furnace, the disulphides are usually recycled to the crude, and the regenerated caustic is circulated to the

extraction column. Figure 2.30 shows a simplified process flow diagram of an extraction process.

Another oxidation process is also a mercaptan oxidation process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic ('mini-alky' operation) are injected into the hydrocarbon stream and the caustic cannot regenerate. As the hydrocarbon passes through the mercaptan oxidation catalyst bed, sulphur mercaptans are oxidised to disulphide.

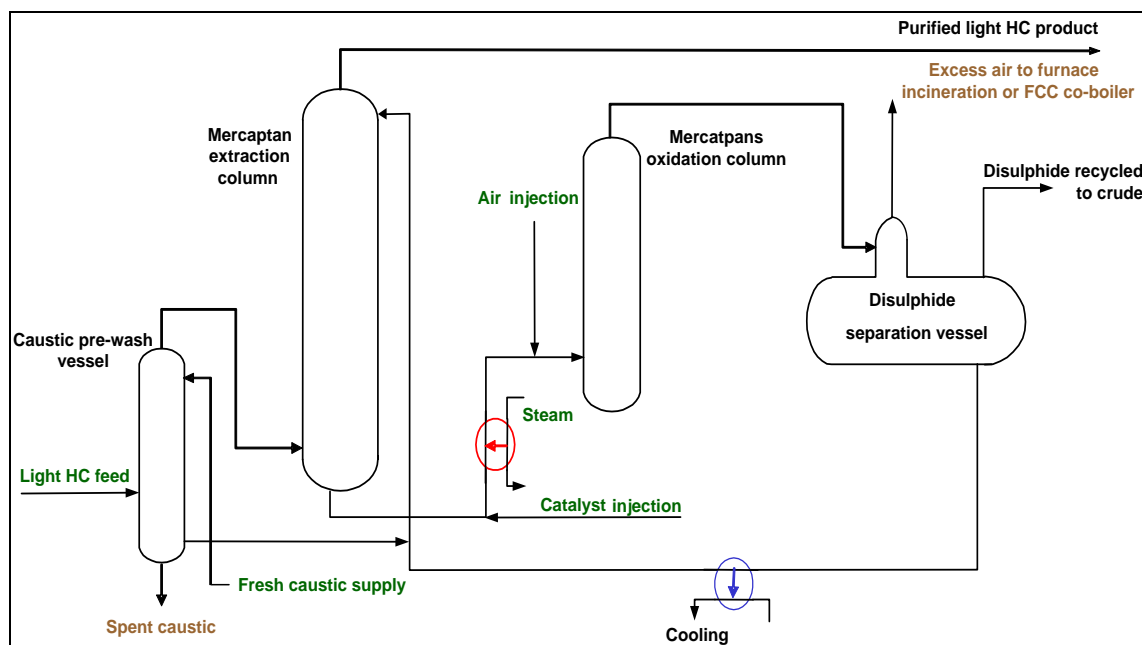


Figure 2.30: Simplified process flow diagram of the mercaptan oxidation extraction process

Both processes can be integrated in a caustic cascading system to achieve the desired product quality improvements at minimum caustic make-up and spent caustic disposal costs.

Figure 2.31 shows a simplified process flow diagram of the mercaptan oxidation extraction process.

Catalytic dewaxing

Another process that can be found in refineries is the selective hydrocracking (hydrofiner), where one or two zeolite catalysts are used to selectively crack the wax paraffins (n- and near-to-n-paraffins). This technique can be used for the dewaxing of mid-distillate components that may be blended into products for extreme winter conditions. A variation of this is the use of isodewaxing catalyst that isomerises the n-paraffin wax to desirable isoparaffin lube molecules, while co-producing low-quality mid-distillate transportation fuels. The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).

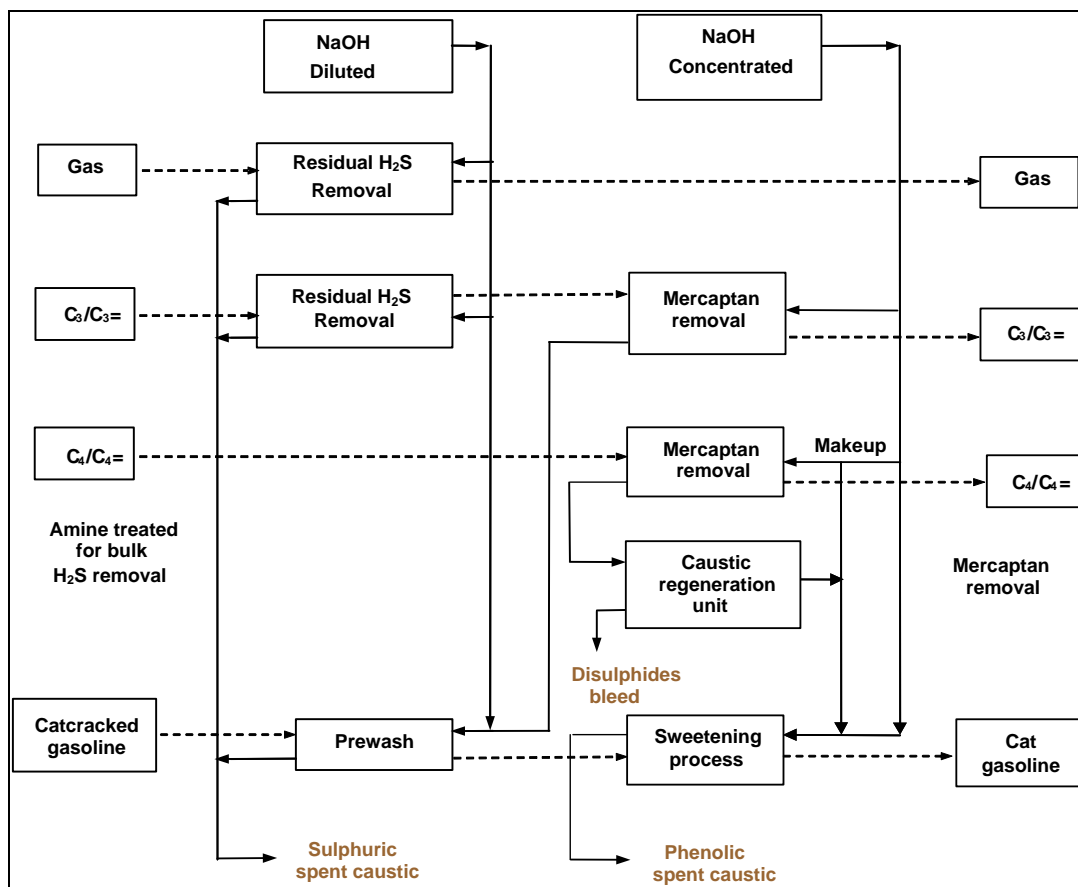


Figure 2.31: Simplified process flow diagram of the caustic cascading system (mercaptan oxidation extraction and sweetening)

2.21 Storage and handling of refinery materials

Storage and handling of refinery materials are not covered exhaustively in this document, because the storage and handling of oil products are within the scope of the horizontal BREF on storage [5, COM 2006], to which reference will be made as appropriate. This section also covers activities related to feed and product blending, piping and other small techniques used for the handling of materials. Storage of specific products, such as base oils, bitumen and petroleum coke, is included in the respective production sections.

Purpose and principle

Crude oil, petroleum intermediates and final products are transferred to, in, and from refineries through marine terminals via pipeline or rail/road vehicles. Between these movements, the products are stored in tanks. Storage tanks or caverns are used throughout the refining process to store crude oil, other raw materials and intermediate process feeds. Finished petroleum products are also kept in storage tanks before transport off site. Tanks are also needed to accommodate the blocked-out operation of processing units and to link continuous refinery processes with discontinuous ones. Consequently, storage is an essential part of a refinery. Blending systems are also used in refineries to prepare feed streams to individual refinery units and to produce finished products to be sold.

Feed blending may be applied to prepare the optimum feed stream to a refinery unit, thereby ensuring the optimum performance of the refinery unit. For example, a refiner processes a mixture of four different low-sulphur crudes in an atmospheric distillation unit. The feed blend is selected so that the throughput in the distillation unit and further downstream units are optimised/maximised, with the objective of maximising overall profit. Alternatively, the different quality crudes may be processed separately for a short period (a few days) in ‘blocked-out’ operations.

Product blending is applied to produce the optimum mix of finished refinery products. The majority of the product streams produced in different refinery units, normally identified as an intermediate product stream, can be blended into more than one finished product stream. For example, (hydrotreated) kerosene product is normally blended into diesel oil, light heating oil and even heavy fuel oil, with the remainder blended into jet fuel oil. The amount of kerosene allocated to the different products is selected so that product demands and specifications are met, with the objective of maximising overall profit. Blending products involves mixing the products in various proportions to meet specifications such as vapour pressure, specific gravity, sulphur content, viscosity, octane number, cetane index, initial boiling point and pour point, and to add distinctive smells (LPG).

Process description

The crude oil storage systems can be located either at a separate oil terminal or within the refinery complex. A large part (often more than 50 %) of the refinery area is occupied by oil movement facilities. Storage tanks can be divided into four main types: pressure vessels, fixed roof tanks, fixed roof tanks with floating covers, and floating roof tanks. Figure 2.32 shows the different types of storage systems found in a refinery.

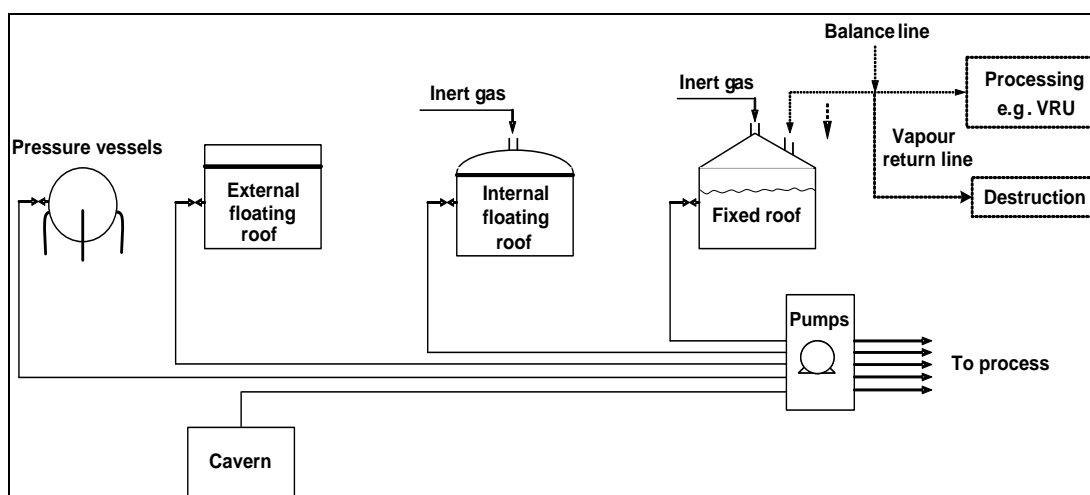


Figure 2.32: Examples of some types of storage tanks

Pressure vessels are normally used to store high-pressure material (>91 kPa), most typically LPG. Fixed roof tanks can hold a wide range of materials. For very low vapour pressure liquids, they can be open to the atmosphere. They can also be designed to hold volatile liquids with several classes of permitted pressure build-up, from 20 mbarg (low pressure) to 60 mbarg (high pressure). In these situations, measures to prevent the occurrence of flammable atmospheres, such as inerting and vapour loss (e.g. floating roof and vapour recovery), are required. Such tanks are necessarily provided with pressure/vacuum relief valves. Fixed roof tanks may also be fitted with internal floating covers. Floating covers float upon and move with the liquid and act as a barrier to evaporation. External floating roof tanks are generally larger and are extensively used for crude oil and product storage.

Above-ground storage tanks (ASTs) are used at refineries for holding either the raw feedstock (crude oil) or end products generated by the refinery processes (gasoline, diesel, fuel oils, etc.). Underground storage tanks are used much less frequently (if at all) at refineries, primarily for storing fuel for on-site boilers and vehicles, or for capturing liquids at low-level drain points. The storage of crude oil and products in caverns is also applicable in some European countries.

Blending can be carried out in-line or in batch blending tanks. An in-line blending system consists of a manifold where individual streams are blended on flow control, and the blend ratio is normally controlled and optimised by a computer. When a certain volume of a given quality product is specified, the computer uses linear programming models to optimise the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost. To ensure that the blended streams meet the desired specifications, in-line stream analysers for flash point, RVP, boiling point, specific gravity, research and motor octane number (RON and MON), sulphur, viscosity, cloud point and others are inserted to provide feedback to the computer, which in turn corrects blending ratios where necessary.

Batch blending involves mixing the feed streams in a blend tank, from where the relevant process units are fed. The same applies to intermediate product streams, which are first sent to intermediate storage tanks, where they are batch blended into the final product tanks.

Additives and odorants.

The odorant is stored as a liquid, normally in fixed tanks. The odorant is not added to the gas stream prior to liquefaction but is usually added to the LPG whilst the LPG is being loaded into the delivery tankers, although in-tank odorising is also carried out. Allowance may be made for any residual mercaptans already present in the LPG. The pump addition rate is carefully controlled. In the case of liquid propane, methanol may be added with the odorising agent in order to prevent hydrate icing in propane evaporators.

Odourising plants are designed to minimise the potential for leaks, e.g. by having the minimum number of pumps/valves/filters/tank connections, etc., by using welded, not flanged, connections wherever possible and by protecting the plant from possible impact damage. All such items used need to be designed to a very high standard of sealing efficiency. Devices such as automatic self-sealing couplings for loading lines are preferred.

Pipes, valves and auxiliary systems, such as vacuum recovery units are found throughout a refinery. Gases, liquids and even solids are transferred from unit operation to unit operation by pipes. Process pipes are normally above ground but some pipes are underground. [147, Irish EPA 1992]

2.22 Visbreaking and other thermal conversions

2.22.1 Visbreaking

Purpose and principle

Visbreaking is a well-established non-catalytic thermal process that converts atmospheric or vacuum residues to gas, naphtha, distillates and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules.

When vacuum residue is directly blended with the heavy fuel oil pool, significant quantities of cutter stock (normally high-value gas oil) need to be blended to the residue to meet the viscosity specifications of the heavy fuel oil. By thermally cracking the vacuum residue at relatively mild conditions, about 10 – 15 % of the feed is cracked to lighter fractions and, more importantly, the viscosity of the vacuum residue is reduced significantly. For this reason, the thermal cracker unit is normally called the ‘visbreaker’ gas oil unit.

Feed and product streams

The atmospheric residue from the crude distillation unit, the vacuum residue from the high vacuum unit, and heavy gas oils or vacuum gas oils or mixtures are typically the feedstocks. In this process, only part of the feedstock is converted and a large amount of residue remains unconverted. As no catalyst is involved in the thermal cracking process, the quality of the feedstock, in terms of metals and sulphur, is not critical. A significant quantity of gas is produced and all distillate products need further treatment and upgrading prior to running them to storage.

Process description

Thermal cracking is one of the oldest conversion processes to upgrade heavy oil fractions. At present, it is mainly used to upgrade vacuum residue. Figure 2.33 shows a simplified process flow diagram of the visbreaker unit. The most important factor in controlling the cracking severity should always be the stability and viscosity of the visbroken residue fed to the fuel oil pool. In general, an increase in the temperature or residence time results in an increase in severity. Increased severity produces higher gas-plus-gasoline yield and at the same time a cracked residue (fuel oil) of lower viscosity. Excessive cracking, however, leads to an unstable fuel oil, resulting in sludge and sediment formation during storage. Thermal cracking converts a maximum 20 % of the feed. Thermal cracking units to upgrade atmospheric residue have conversion levels significantly higher (35 – 45 %) and the viscosity of the atmospheric residue is reduced.

The feedstock is heated above 500 °C and then fed to a reaction chamber, which is kept at a pressure of about 9.65 barg. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporise and are drawn off. The lighter products are fed to a fractionating tower, where the various fractions are separated. The bottoms consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel.

There are two types of visbreaker operations, ‘coil or furnace cracking’ and ‘soaker cracking’. Coil cracking uses higher furnace outlet temperatures (470 – 500 °C) and reaction times from one to three minutes, while soaker cracking uses lower furnace outlet temperatures (430 – 440 °C) and longer reaction times. The product yields and properties are similar. Run times of three to six months are common for furnace visbreakers and six to eighteen months for soaker visbreakers.

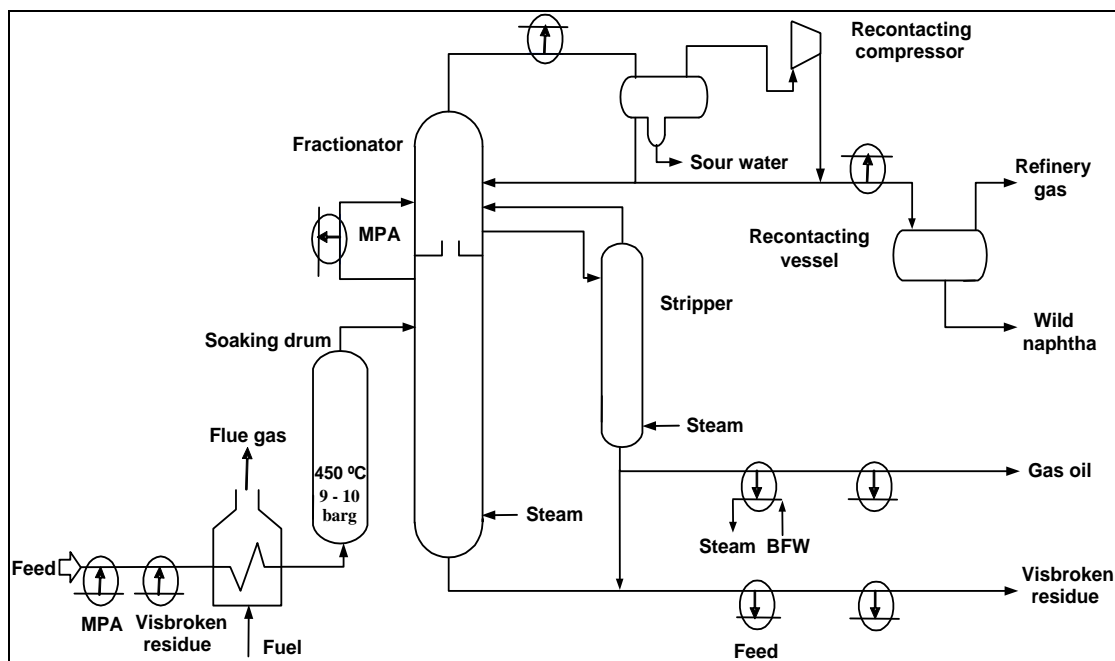
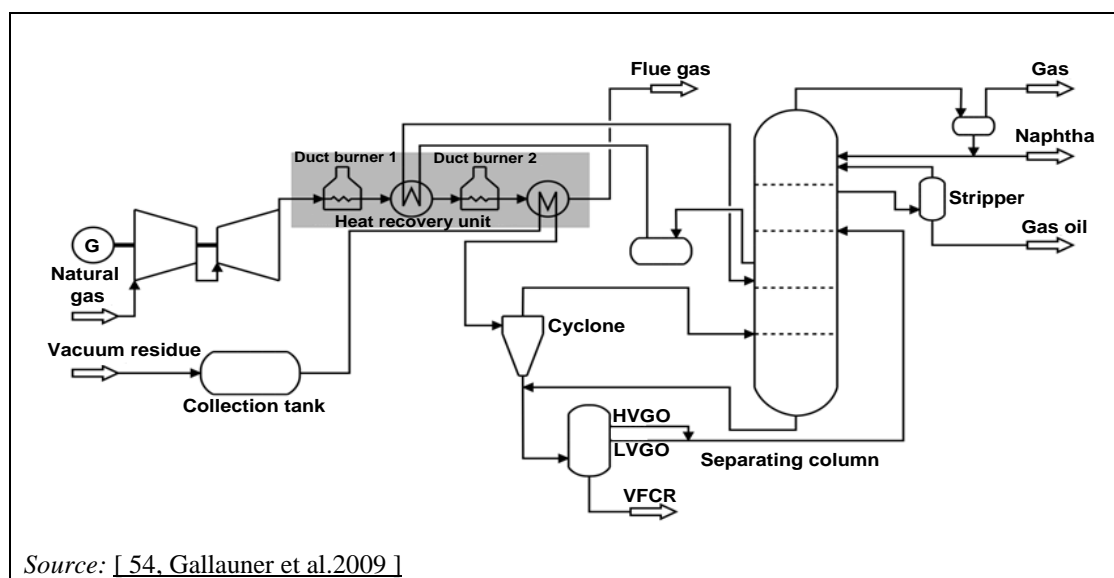


Figure 2.33: Simplified process flow scheme for a visbreaking unit

2.2.2.2 Thermal gas oil unit

The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gas oil and naphtha cuts produced. As shown in Figure 2.34, after a first thermal cracking, the resulting products are separated in a cyclone. The gaseous phase is introduced in the flash zone of the main distillation column and separated according to the desired boiling intervals. The heavy gas oil (HVGO) and the vacuum gas oil from the flash column (LVGO) are treated in a second thermal cracker and reintroduced into the column.



Source: [54, Gallauner et al.2009]

Figure 2.34: Simplified process of a thermal gas oil unit

The resulting vacuum flashed cracked residue (VFCR) has a high sulphur content and can only be used as fuel in the refinery power plant if equipped with an efficient and appropriately sized flue-gas cleaning system.

2.23 New high conversion techniques

Residue upgrading has great importance among refiners due to a continued decrease in demand for high sulphur fuel oil (HSFO) and a great demand for higher volumes and quality of middle distillates. In addition, the price differential between light/sweet and heavy/sour crudes is driving operators to process larger volumes of heavy crudes.

Refiners and engineering firms aim to minimise fuel oil production at minimum investment and operating costs. The technology options available for residue upgrading depend on the difficulty of the feed to be processed, whether it is atmospheric (AR) or vacuum residue (VR), the metal contents and the level of conversion desired.

There has not been any technology breakthrough, only marginal improvements on proven technologies. Final results will depend on how the integration within units is done.

The following tables summarise those processes that have experienced recent improvements regarding residue conversion and/or valorisation.

Table 2.12: Conversion techniques grouped by feed and chemical engineering approach

| Feed | Carbon rejection | H ₂ addition | Partial oxidation |
|----------------|--------------------------------------|-----------------------------------|-------------------|
| Vacuum GO | FCC | H ₂ Cracking | |
| Vacuum Residue | Coking Visbreaking SDA RFCC | ARDS/VRDS H-Oil HCK HDHplus | Gasification |

Source: EIPPCB review

Table 2.13: Examples of recent improvements made by several conversion techniques

| BREF Section | Technique names | Technical description | Advantage | Drawbacks |
|--------------|------------------------------------|---|---|--|
| 3 | Solvent Deasphalting | Separates by molecular weight | Separates residue from deasphalted oil | High post-treatment |
| 5 | FCC upgrade | Better catalysts enable heavier/wider feedstocks | | |
| | Residue FCC/Deep CC | Fluidised process, two-stage regenerator | Cost-effective | |
| 7 | Delayed Coker | Low-pressure low recycling, low coke | High flexibility and high conversion to lighter | Uses much water; harder to sell coke at fair price and high capital cost |
| 10 | IGCC/Gasification | | Valorisation of waste to syngas | |
| 10 | Circulating Fluid Bed Boiler (CFB) | Coke valorisation at low emission | Possible cogeneration | Solid handling |
| 13 | Atmospheric residue DS | Optimised catalyst combination | | High investment and Ops cost |
| 13 | Vacuum residue DS | Higher ppH ₂ | | High investment and Ops cost |
| 13 | Slurry HC | Disperse phase catalyst and elevated temp | Selective conversion, minimum residue | |
| 13 | Residue HC/ebullated bed HC | Fixed bed+HT catalysts | Reduces metals, sulphur, CCR, produces high distillates | |
| 22 | Visbreaking | Rapid heat in furnace and cracked for a specific residence time in a soaking zone | Reduces viscosity, lower capital cost | High post-treatment, low conversion to light |
| 22 | Thermal GO/deep thermal conversion | Lower temp, special internal for backmixing | Selective cracking, lower investment cost | |

2.24 Techniques for the elimination and the valorisation of external waste used as a secondary raw material

There is an increasing role played by the refineries in recycling waste oil, not only managing their own residues but also valorising external waste.

Some wastes are partly used as feedstock in the EU refineries, as follows:

- Re-refining of waste oil

Used oil from different applications is first collected and then part of it is sent back to refineries. In 2006, in the EU, this recycling effort represented only 0.1 % of the crude oil feedstock, however this initiative is growing.

The largest group of end users that are recycling oil are auto repair shops, large industrial consumers of lubricants (e.g. ironworks, mines, power plants and electricity distribution networks), and large transportation fleets. Table 2.14 shows the order of magnitude by quantities by country.

- Recycling of waste rubber of asphalt grades

There is a large volume of spent tyres in the EU. In some processes, tyres are converted into powder and then mixed with asphalt grades.

- Waste oil hydrogenated in refineries

For a more in-depth description, see Chapter 6, (hydro)isomerisation. There are some examples of the recycling of animal and vegetable oil (waste) using retrofitted desulphurisation units: e.g. Cepsa (Spain) started in 2011 and plan a 100 000 m³/year production. Oil is hydrogenated and then mixed in diesel gasoline grades.

Table 2.14: Re-refining waste oil in Europe

| Member State | Collected waste oil in 2006 (tonnes) | Distillation of waste oil (tonnes) | | | |
|----------------|--------------------------------------|------------------------------------|--------------------------|---------------------------------------|----------------|
| | | Refining (base oil) | Burning (replacing coal) | Burning (replacing heavy fuel oil)(*) | Other/ unknown |
| Austria | 39 596 | 12 396 | 24 700 | 2 500 | |
| Belgium | 60 000 | 15 000 | 500 | 25 000 | 19 500 |
| Bulgaria | 17 000 | | | 1 200 | 15 800 |
| Cyprus | 4 300 | | | 4 300 | |
| Czech Republic | 32 867 | 986 | 4 800 | 27 081 | |
| Denmark | 20 000 | 15 500 | 2 000 | 2 500 | |
| Estonia | 5 400 | | 11 250 | 2 700 | |
| Finland | 22 500 | | 39 130 | 11 250 | |
| France | 224 759 | 99 403 | 70 000 | 61 439 | 24 787 |
| Germany | 525 000 | 135 000 | | 295 000 | 25 000 |
| Greece | 36 000 | 36 000 | | | |
| Hungary | 27 823 | | 6 000 | 7 823 | 14 000 |
| Ireland | 20 000 | | | | 20 000 |
| Italy | 216 300 | 172 600 | | 34 600 | 9 100 |
| Latvia | 11 000 | | 5 500 | 5 500 | |
| Lithuania | 14 000 | | 7 000 | 7 000 | |
| Luxembourg | 5 364 | 5 364 | | 0 | |
| Malta | 1 200 | | | | 1 200 |
| Netherlands | 50 000 | 18 000 | | 32 000 | |
| Poland | 76 500 | 63 500 | 3 000 | 10 000 | |
| Portugal | 28 700 | 6 800 | 3 550 | 13 550 | 4 800 |
| Romania | 27 663 | | 9 500 | 16 147 | 2 016 |
| Slovenia | 3 967 | | | 3 499 | 468 |
| Slovakia | 15 000 | | 6 000 | 9 000 | |
| Spain | 216 045 | 140 084 | | 74 362 | 1 599 |
| Sweden | 45 000 | 8 000 | 37 000 | | |
| United Kingdom | 350 000 | | | 270 000 | 80 000 |
| | | | | | |
| Total: | 2 095 984 | 728 633 | 232 630 | 916 451 | 218 270 |
| Percentage (%) | 100 % | 35 % | 11 % | 44 % | 10 % |

(*) Including direct burning and simple treatment.
Source: GEIR 2008 quoted by Oköpol – 2008

2.25 Techniques for the abatement of emissions

There are many non-production techniques in use in a refinery. Particularly relevant, for this document, are those techniques used to control and abate emissions to air, water and soil. Descriptions of many of these techniques can be found in the CWW BREF [6, COM 2003] [\[REFERENCE BOOKMARK 8787\]](#). These techniques are not described in this chapter because they are typically techniques that might be considered in the determination of BAT and consequently are extensively described and analysed in Chapter 4 (see Sections 4.23 and 4.24).

Even if some preventive techniques or primary measures can also be implemented, pollutants such as NO_x, particulates, H₂S, SO₂, other sulphur compounds and VOCs, among others, are typically abated by end-of-pipe techniques. One of the largest systems within a refinery is the abatement of H₂S produced on site. These systems typically contain an amine scrubbing system and a sulphur recovery unit to convert H₂S into sulphur, a by-product produced within refineries.

Flares are another technique used within the refinery for safety and environmental reasons. Techniques for the abatement of odour and noise are also relevant for refineries. Specific information on flare systems can be found in the CWW BREF [6, COM 2003].

Most refineries treat waste water on site using end-of-pipe waste water treatment facilities prior to discharge. However, several refineries utilise off-site waste water treatment services. Both on-site and off-site waste water treatment facilities reduce the amounts of pollutants that are discharged into the receiving environment.

Refineries also generate solid wastes. Some of them are recycled within the refinery, others (e.g. catalysts) are recycled by specialist companies and others are disposed of. Soil contamination prevention techniques are also relevant to the whole refinery.

3 CURRENT EMISSION AND CONSUMPTION LEVELS

This chapter provides data and information about current emission and consumption levels in existing installations at the time of writing (2009 – 2013). Because it covers many types and sizes of refineries, the data are very wide-ranging. The goal of the chapter is to bring together the emission and consumption levels of the refinery as a whole and for each specific process. The data cited will, in most cases, enable an estimate of the concentration and load of emissions, in turn enabling a competent authority issuing a permit to verify the information provided in the permit application.

Section 3.1 gives an overview of the main emissions and consumption of European refineries as a whole. It is not a simple aggregation of the emissions and consumption in the other sections: most of them cannot be aggregated because of the varying integration of processes in refineries.

Sections 3.2 to 3.22 cover the emissions and consumption from the various processes/activities covered by this document. Sections 3.23 to 3.25 cover the emissions generated by the techniques used to abate emissions, including the emissions from sulphur recovery units. The chapter ends with a section on monitoring, which covers the monitoring systems typically applied in refineries and provides some discussion on their application.

3.1 Current emission and consumption levels in refineries as a whole

Refineries are industrial sites that manage huge amounts of raw materials and products and are also intensive consumers of energy and water. From storage and the refining process they generate emissions to the atmosphere and to water and they may also potentially pollute the soil.

This chapter addresses these three media, and the pollutants that affect them, and is a summary of the emissions from all refinery processes. The main environmental problems were mentioned in Chapter 1 (Section 1.4), but without figures. This section aims to quantify refinery emissions.

Although the principal raw material input to petroleum refineries is crude oil, refineries use and generate a large number of chemicals, some of which leave the facilities as discharges of air emissions, waste water or solid waste. Pollutants generated typically include ammonia (NH₃), carbon dioxide (CO₂), carbon monoxide (CO), hydrogen sulphide (H₂S), metals, nitrogen oxides (NO_x), particulates, spent acids (e.g. HF, H₂SO₄), sulphur oxides (SO_x), volatile organic compounds (VOC) and numerous other organic compounds.

Figure 3.1 shows a simplified example of what is consumed and emitted by a refinery. This figure only focuses on the main typical pollutants, among more than 90 specific compounds that have already been identified as likely to be generated by refining processes and activities [161, USAEPA 1995]. The great majority are pollutants to air. In this figure, low values in the ranges normally correspond to refineries with abatement techniques and good environmental performance and practices, whereas high values typically correspond to refineries without abatement techniques.

Table 3.1 shows the environmental accounts of refinery processes, and provides a summary of the impact on the different media from the different activities found within refineries.

Table 3.1: Environmental accounts of refinery processes

| Process/Functional unit | Environmental item | | | | | | |
|---|--------------------|-------------|-------|-----------------------|------------|-------|--------|
| | Air | Waste water | Waste | Substances and energy | Waste heat | Noise | Safety |
| Fundamental processes | | | | | | | |
| Delivery | — | — | — | — | — | 0 | X |
| Loading | X | — | — | — | — | X | X |
| Storage | X | 0 | X | 0 | 0 | — | X |
| Process furnaces | X | — | 0 | X | X | X | X |
| Separation processes | | | | | | | |
| Crude oil atmospheric distillation unit | X | X | 0 | X | X | 0 | X |
| Vacuum distillation unit | X | X | 0 | X | X | 0 | X |
| Gas separation unit | X | 0 | 0 | 0 | 0 | 0 | X |
| Conversion processes | | | | | | | |
| Thermal cracking, visbreaking | X | X | 0 | X | X | 0 | X |
| Delayed coking | X | X | X | X | X | X | X |
| Catalytic cracking | X | X | X | X | X | 0 | X |
| Hydrocracking | X | X | X | X | X | 0 | X |
| Bitumen blowing | X | X | X | X | X | 0 | X |
| Reforming | X | X | X | X | X | 0 | X |
| Isomerisation | X | X | X | X | X | 0 | X |
| MTBE production | X | X | X | X | 0 | 0 | X |
| Alkylation | X | 0 | X | X | 0 | 0 | X |
| Refining processes | | | | | | | |
| Hydrosulphurisation | X | X | X | X | X | 0 | X |
| Sweetening | X | X | X | X | 0 | 0 | X |
| Gas washing | X | 0 | X | X | 0 | 0 | X |
| Lubricating oil production | X | X | X | X | 0 | 0 | X |
| Extractions | | | | | | | |
| - with solvents | X | 0 | 0 | X | 0 | — | X |
| - with molecular sieves | X | — | X | X | 0 | — | X |
| Other processes | | | | | | | |
| Sulphur plant | X | X | 0 | 0 | 0 | 0 | X |
| Flare | X | X | 0 | 0 | 0 | X | X |
| Cooling tower | X | X | 0 | 0 | 0 | 0 | 0 |
| Waste water treatment | X | X | X | X | 0 | — | 0 |
| Blending units | X | X | 0 | 0 | 0 | — | X |
| Off-gas clean-up (Exhaust gas recovery unit) | X | X | X | 0 | 0 | 0 | X |
| NB: X: high impact 0: small impact —: very small or no impact | | | | | | | |
| Source: [222, UBA 2000] | | | | | | | |

3.1.1 Present consumption levels in refineries

3.1.1.1 Energy

General information

Petroleum refining is one of the most energy-intensive industries. In a country like the US, refining activities account for 28 % of the energy consumed by industry.

Energy is required by the combustion systems and process units. The largest energy use is of internal or external fuels in a combustion plant, which can be up to 200 MW thermal input in size. Some refineries use Combined Heat and Power (CHP) units to raise some of their steam and electricity. Such units may be operated by third parties and export some of their energy. Also, they may use commercial rather than internal refinery fuels. Processes such as catalytic cracking can provide energy from the burn-off of coke, usually supplemented by internal fuel for efficient heat recovery. Sulphur removal from products is energy-intensive as it requires hydrogen production.

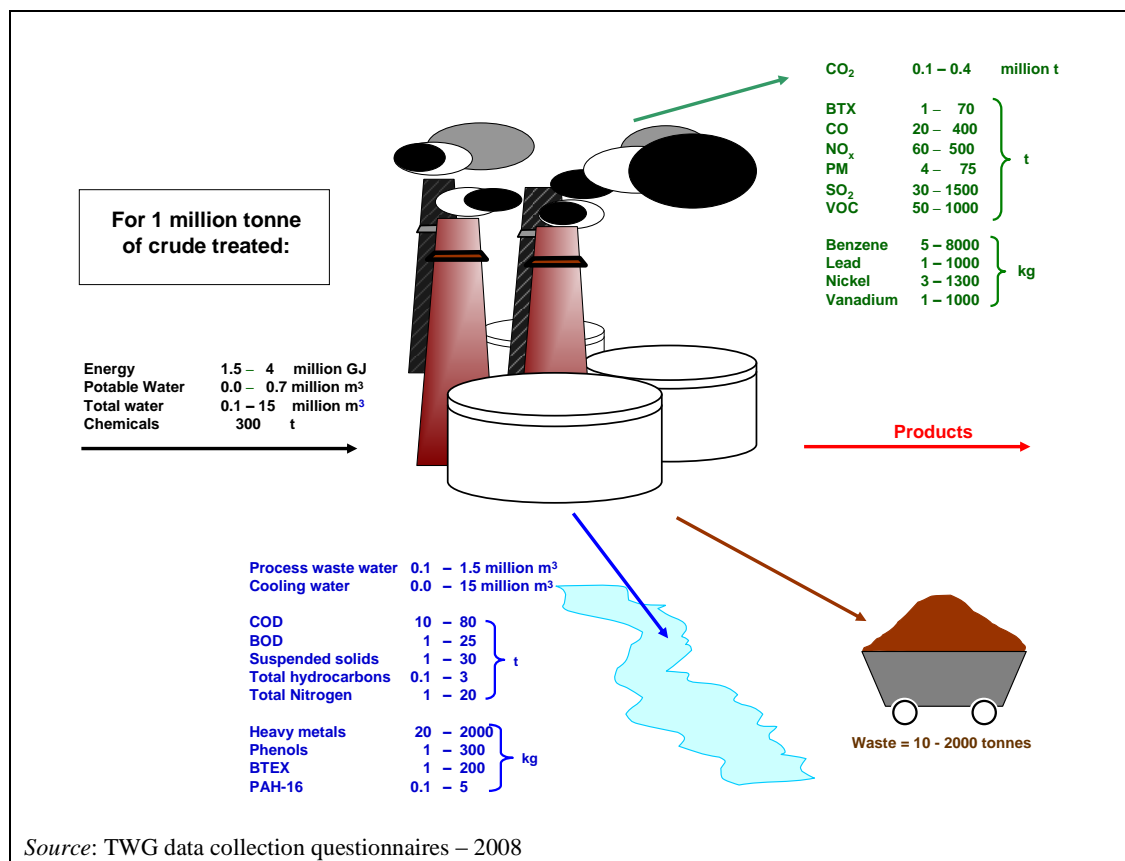


Figure 3.1: Example of specific emissions and consumption in European refineries

The actual specific consumption levels of a sample of European refineries in recent years are shown in Table 3.2, ranging from 1.5 GJ/t to 4.0 GJ/t of crude, with an average of 2.75 GJ/t. Around 3 – 9 % of the crude feedstock received is burnt in the refinery. As shown in Figure 3.3, the site's overall CO₂ emissions are rather narrowly correlated to specific consumption.

Growing impact of desulphurisation processes

Processes that have the greatest throughput dominate energy consumption; atmospheric distillation and, to a lesser extent, vacuum distillation units represent together 35 – 40 % of the total process energy consumed in a refinery. However, it can be noted from Figure 3.2 that energy consumption is also clearly related to the sulphur input recovered from the overall refinery feedstock, linked to the fact that, on average, another 20 – 25 % of this energy is spent in hydrotreating.

Figure 3.2 gives the distribution of energy consumption for each main process typically operated in US refineries, calculated as an average from the 146 refineries that were operated in 2001 [68, Worrell et al.2005]. In this graphic, all data are expressed in primary energy (see the graphic footnotes).

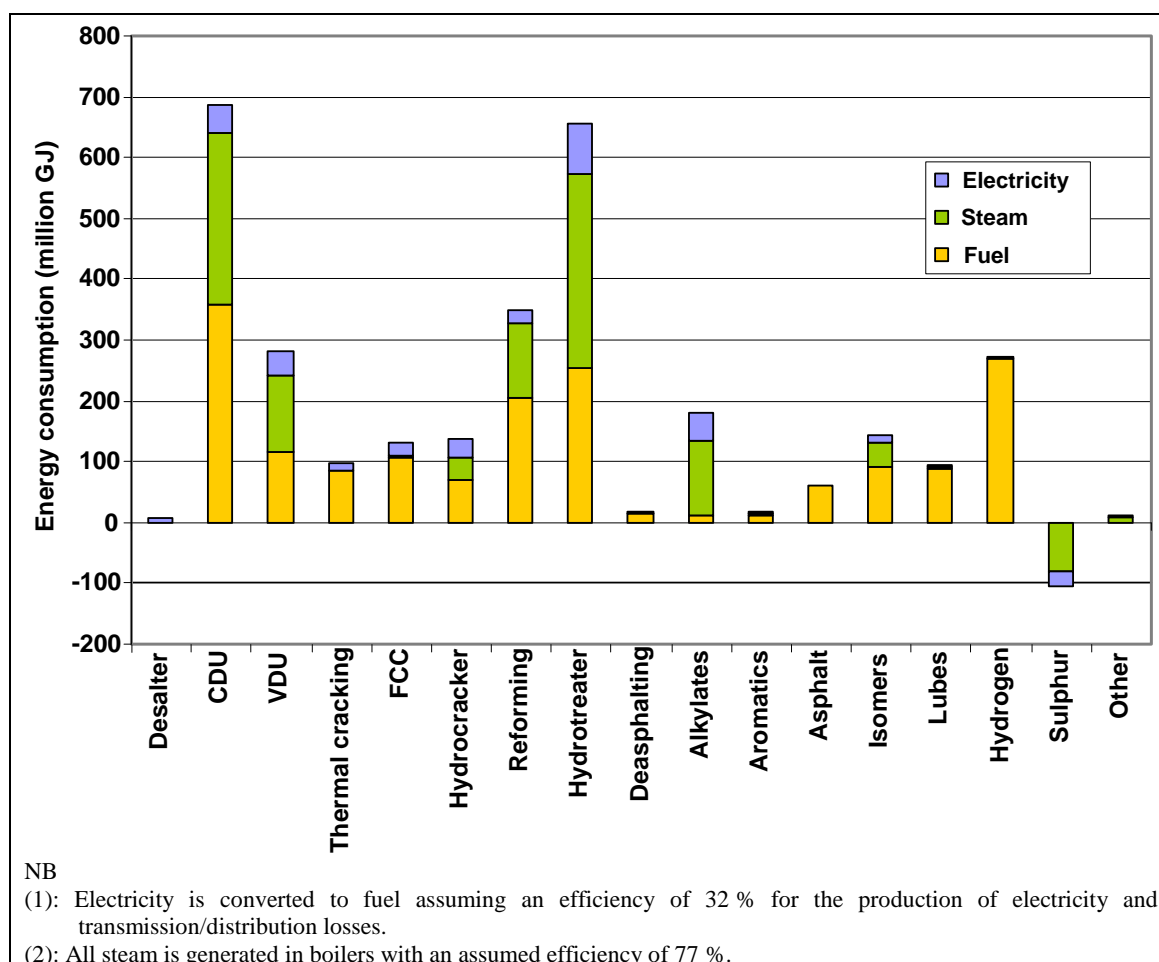


Figure 3.2: Estimated primary energy consumption distributed by refining process in the US

Impact of site complexity

It is interesting to notice in Figure 3.3 that, despite quite a large dispersion of values, there is also a clear general trend for most complex sites to be associated with highest specific energy consumption levels.

Use of natural gas

A growing part of necessary energy comes from the supply of external fuels, especially natural gas which is used in 31 out of these 48 refineries (64.5 % of the sample). Natural gas represents on average 17 %, and up to 82 %, of the overall consumption of the sites concerned. As shown in Figure 3.4, there is no obvious correlation between the part of total gaseous fuels (RFG + eventual external supply of natural gas) and the specific energy consumption. However, refineries where natural gas is the most intensively used are usually operating recent CHP plants for their steam delivery; it is then not surprising that the largest natural gas use closely correlates with the best specific energy consumption levels.

Table 3.2: Specific energy consumption and other relevant data for a selection of EU refineries

| Questionnaire label | Nelson Index | Total feedstock refined | Net thermal energy used | Specific energy consumption | Specific CO ₂ emission | Natural gas/total energy | Total gaseous fuels/total energy | S emitted/S input (%) |
|-------------------------|--------------|-------------------------|-------------------------|-----------------------------|-----------------------------------|--------------------------|----------------------------------|-----------------------|
| N° | | kt | 10 ⁶ GJ | GJ/t | t/t | % | % | % |
| 1 | 6.2 | 9096 | 42.04 | 4.6 | 0.31 | 7 % ^(*) | 52 % ^(*) | NA |
| 2 | 11.2 | 606 | NA | NA | 0.28 | 1 % | 6 % | 3.8 % |
| 3 | 5.7 | 3483 | 5.85 | 1.7 | 0.13 | 0 % | 92 % | 5.3 % |
| 4 | 3.1 | 4900 | 8.37 | 1.7 | 0.10 | 0 % | 100 % | 0.8 % |
| 5 | 6.8 | 2772 | 5.75 | 2.1 | 0.15 | 0 % | 100 % | 2.0 % |
| 6 | 13.5 | 12400 | 43.26 | 3.5 | 0.24 | 82 % | 89 % | 2.2 % |
| 7 | 6.4 | 3268 | 7.05 | 2.2 | 0.15 | 0 % | 96 % | 5.9 % |
| 8 | | 953 | 3.25 | 3.4 | 0.27 | 35 % | 35 % | 5.9 % |
| 9 | 6.6 | 5727 | 12.11 | 2.1 | 0.14 | 3 % | 86 % | 4.9 % |
| 10 | 6.8 | 8852 | 22.13 | 2.5 | 0.16 | 8 % | 67 % | 7.5 % |
| 11 | 6.2 | 9350 | 20.41 | 2.2 | 0.16 | 10 % | 68 % | 4.9 % |
| 12 | 9.0 | 6412 | 20.77 | 3.2 | 0.22 | 0 % | 61 % | 13.4 % |
| 13 | 6.0 | 5303 | 16.45 | 3.1 | 0.25 | 3 % | 74 % | 11.2 % |
| 14 | 9.3 | 16552 | 60.95 | 3.7 | 0.24 | 41 % | 85 % | 5.2 % |
| 15 | 6.9 | 4858 | 12.09 | 2.5 | 0.15 | 0 % | 73 % | 10.8 % |
| 16 | 8.7 | 7153 | 21.01 | 2.9 | 0.17 | 9 % | 78 % | 6.2 % |
| 17 | 4.0 | 728 | 1.94 | 2.7 | 0.23 | 0 % | 63 % | 10.2 % |
| 18 | 12.9 | 8272 | 19.05 | 2.3 | 0.17 | 28 % | 100 % | 0.8 % |
| 19 | 5.1 | 3359 | NA | NA | 0.11 | NA | NA | NA |
| 20 | 12.9 | 9243 | 28.92 | 3.1 | 0.22 | 13 % | 71 % | 4.9 % |
| 21 | 13.1 | 5627 | 43.05 | 7.7 | 0.69 | 1 % | 29 % | 3.5 % |
| 22 | 7.2 | 8635 | 25.71 | 3.0 | 0.25 | 4 % | 89 % | 3.0 % |
| 23 | 8.4 | NA | NA | NA | NA | 0 % | 92 % | NA |
| 24 | 4.9 | 8653 | 5.84 | 0.7 | 0.10 | 0 % | 54 % | 2.7 % |
| 25 | 9.7 | 3613 | 7.84 | 2.2 | 0.14 | 34 % | 97 % | 0.5 % |
| 26 | 10.8 | 10193 | 28.10 | 2.8 | 0.23 | 2 % | 84 % | 1.1 % |
| 27 | 10.8 | 19151 | 68.50 | 3.6 | 0.29 | 29 % | 78 % | 2.5 % |
| 28 | 9.4 | 14251 | 50.25 | 3.5 | 0.26 | 41 % | 54 % | 2.6 % |
| 29 | 9.4 | 3817 | 13.80 | 3.6 | 0.27 | 0 % | 41 % | 13.9 % |
| 30 | 6.3 | 10490 | 24.07 | 2.3 | 0.20 | 2 % | 50 % | 4.4 % |
| 31 | 6.7 | 12087 | 31.34 | 2.6 | 0.17 | 0 % | 64 % | 3.7 % |
| 32 | 11.4 | 5886 | 14.23 | 2.4 | 0.20 | 29 % | 74 % | 4.5 % |
| 33 | 4.6 | 4610 | 9.43 | 2.0 | 0.14 | 0 % | 46 % | 3.0 % |
| 34 | 8.6 | 10462 | 28.81 | 2.8 | 0.23 | 7 % | 58 % | 3.8 % |
| 35 | 5.7 | 3624 | 9.74 | 2.7 | 0.18 | 27 % | 51 % | 7.0 % |
| 36 | 10.1 | 5622 | 17.63 | 3.1 | 0.24 | 0 % | 46 % | 4.1 % |
| 37 | 9.5 | 7293 | 22.02 | 3.0 | 0.22 | 17 % | 67 % | 3.3 % |
| 38 | 7.3 | 8183 | 20.44 | 2.5 | 0.17 | 4 % | 59 % | 7.4 % |
| 39 | 8.2 | 10098 | 22.98 | 2.3 | 0.18 | 0 % | 99 % | 0.2 % |
| 40 | 6.2 | 5668 | 9.45 | 1.7 | 0.10 | 7 % | 89 % | 0.6 % |
| 41 | 6.5 | 3942 | 9.10 | 2.3 | 0.13 | 0 % | 100 % | 0.3 % |
| 42 | 12.0 | 10916 | 28.64 | 2.6 | 0.17 | 3 % | 100 % | 6.2 % |
| 43 | 8.7 | 15474 | 46.57 | 3.0 | 0.20 | 22 % | 70 % | 7.9 % |
| 44 | 1.6 | 4410 | NA | NA | 0.59 | 0 % | 1 % | 5.2 % |
| 45 | 8.4 | 10050 | 37.80 | 3.8 | 0.27 | 0 % | 59 % | 18.9 % |
| 46 | 6.2 | 9712 | 24.42 | 2.5 | 0.18 | 20 % | 82 % | 8.6 % |
| 47 | 11.6 | 11871 | 25.19 | NA | 0.20 | 0 % | 76 % | 11.6 % |
| 48 | 8.4 | 6900 | 10.85 | 1.6 | 0.53 | 0 % | 44 % | 1.7 % |
| 49 | 5.7 | 15000 | 32.00 | 2.1 | 0.14 | 25 % | 100 % | 3.2 % |
| 50 | 10.5 | 4620 | 13.88 | 3.0 | 0.20 | 0 % | 95 % | 4.5 % |
| 51 | 8.4 | 4400 | 14.40 | 3.3 | 0.22 | 6 % | 95 % | 8.4 % |
| 52 | 10.9 | 4990 | 9.77 | 2.0 | 0.26 | 3 % | 89 % | 4.7 % |
| 53 | 3.8 | NA | 6.20 | NA | NA | 0 % | 91 % | NA |
| 54 | 5.4 | 10794 | NA | NA | 0.15 | NA | NA | NA |
| 55 | 5.1 | 940 | NA | NA | NA | 0 % | 25 % | 0.7 % |
| 56 | 12.4 | 6276 | 11.81 | 1.9 | 0.18 | 3 % | 48 % | 3.0 % |
| Number of values | 56 | 55 | 54 | 50 | 48 | 53 | 53 | 51 |

| | Total feedstock refined | Net thermal energy used | Specific energy consumption | Specific CO ₂ emission | Natural gas/total energy | Total gaseous fuels/total energy | S emitted/S input (%) |
|-----------------|-------------------------|-------------------------|-----------------------------|-----------------------------------|--------------------------|----------------------------------|-----------------------|
| | kt | 10 ⁶ GJ | GJ/t | t/t | % | % | % |
| Minimum | 606 | 2 | 0.67 | 0.10 | 0.0 % | 0.9 % | 0.2 % |
| Maximum | 19 151 | 69 | 7.65 | 0.69 | 82.3 % | 100 % | 18.9 % |
| Average | 7 436 | 22 | 2.75 | 0.22 | 9.8 % | 70.5 % | 5.1 % |
| Sum | 401 544 | 1075 | | | | | |
| 5th Percentile | | | 1.67 | 0.106 | 0.0 % | 27.4 % | 0.6 % |
| 95th Percentile | | | 3.73 | 0.395 | 37.1 % | 100 % | 12.5 % |

NA: these data have not been made available to the TWG.
Source: TWG data collection for 2008 except (*) 2009

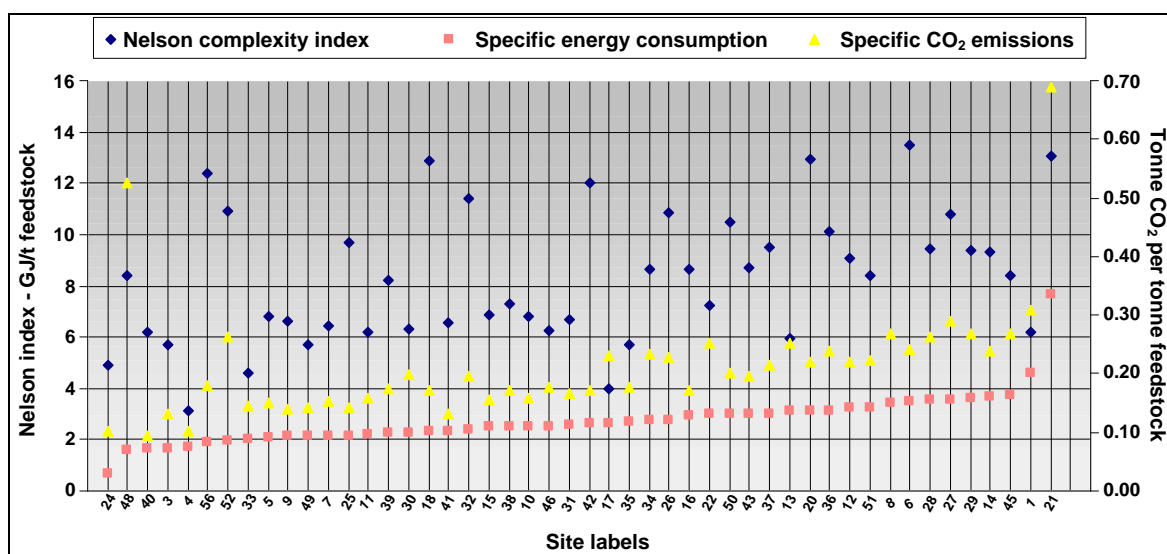


Figure 3.3: Specific energy consumption compared to CO₂ emissions and site complexity for a sample of EU refineries

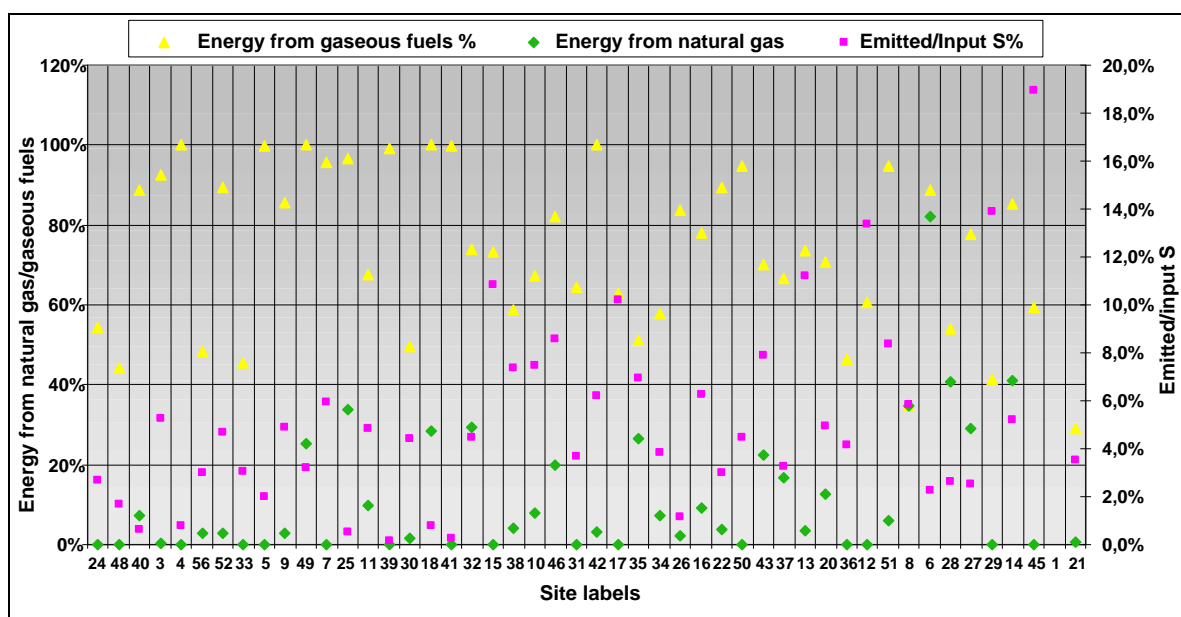


Figure 3.4: Use of gaseous fuels and emitted part of sulphur input for a sample of EU refineries sorted by ascending order of specific energy consumption

3.1.1.2 Water

Water and steam are mainly used:

- in the various refinery processes, to assist the distillation process or the cracking of hydrocarbons, in overhead systems, and for washing, scrubbing, quenching or (steam) stripping. The desalter is the biggest user, and the main producer of waste water in oil refineries (with the exception of base oil refineries);
- for tank and flare seal drains;
- for cleaning operations;
- for steam generation as a feedstock for boilers and CHPs;
- for cooling systems.

From a qualitative point of view, the first three categories of use generate the main part of the organic load which must be abated in the WWTP, since the water will have been in direct contact with hydrocarbons and is usually contaminated. This type of water is typically referred to as process water. On the other hand, from a quantitative point of view, the amount of water used depends primarily on the type of refinery and, especially, on the cooling systems used: closed, open recirculating, or once-through systems.

Actual specific usages of water of a sample of European refineries are displayed in Table 3.3. Most of it (90 % of the data - from the 5th to 95th percentiles) ranged between 0.2 m³/t and 25 m³/t of feedstock refined. The largest part (more than 50 % on average) is still used for cooling. As well, as shown in Figure 3.5, the highest specific usages (above 1 m³/t) at the site level are always determined by the highest cooling usage. They relate to sites where the greatest proportion of once-through cooling circuits are still used.

Potable water from public supply represents, on average, 3 % of the overall usage of these refineries, but its use varies greatly. Some sites do not use any potable water, while other sites fully rely upon it, including for purposes other than sanitary use.

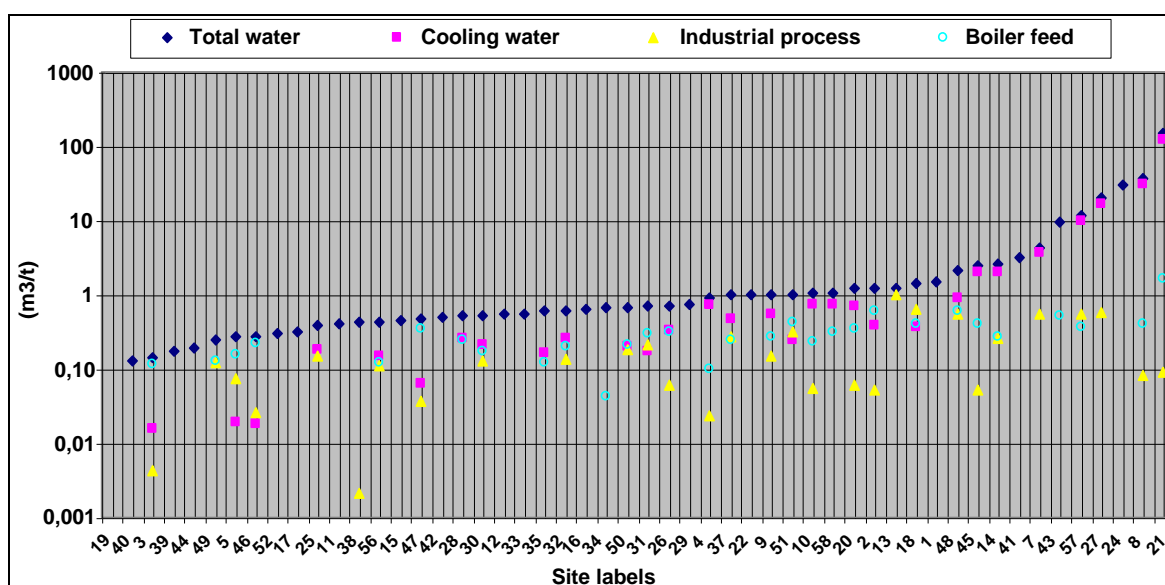


Figure 3.5: Specific water usage data for a selection of European refineries

Table 3.3: Water consumption data for a set of European refineries

| Site label | Nelson Index | Total water consumed | Specific water consumption | Water for industrial processes | | | Water for boilers feed | | | Water for cooling systems | | | Proportion of use of fresh water | | |
|------------|--------------|----------------------|----------------------------|--------------------------------|--------|-------------------|------------------------|------|-------------------|---------------------------|------|-------------------|----------------------------------|--------|-------------------|
| | | Mm ³ /yr | m ³ /t | m ³ /yr | % | m ³ /t | m ³ /yr | % | m ³ /t | m ³ /yr | % | m ³ /t | m ³ /yr | % | m ³ /t |
| 1 | 6.2 | 13.50 | 1.48 | NA | | | NA | | | NA | | | NA | | |
| 2 | 11.2 | 0.74 | 1.22 | 31 000 | 4.2 % | 0.05 | 360 000 | 49 % | 0.59 | 235 000 | 32 % | 0.39 | 41 750 | 5.6 % | 0.07 |
| 3 | 5.7 | 0.50 | 0.14 | 15 000 | 3.0 % | 0.004 | 412 000 | 83 % | 0.12 | 55 000 | 11 % | 0.02 | 495 500 | 100 % | 0.14 |
| 4 | 3.1 | 4.42 | 0.90 | 117 000 | 2.6 % | 0.02 | 500 000 | 11 % | 0.10 | 3 780 000 | 86 % | 0.77 | 25 000 | 0.6 % | 0.01 |
| 5 | 6.8 | 0.74 | 0.27 | 204 000 | 27.5 % | 0.07 | 432 000 | 58 % | 0.16 | 54 000 | 7 % | 0.02 | 743 000 | 100 % | 0.27 |
| 7 | 6.4 | 13.65 | 4.18 | 1 802 816 | 13.2 % | 0.55 | NA | | | 11 808 517 | 86 % | 3.61 | 41 200 | 0.3 % | 0.01 |
| 8 | NA | 35.81 | 37.56 | 79 504 | 0.2 % | 0.08 | 383 091 | 1 % | 0.40 | 34 845 753 | 97 % | 36.55 | 463 677 | 1.3 % | 0.49 |
| 9 | 6.6 | 5.79 | 1.01 | 873 560 | 15.1 % | 0.15 | 1 581 120 | 27 % | 0.28 | 3 162 240 | 55 % | 0.55 | 0 | 0.0 % | 0.00 |
| 10 | 6.8 | 9.20 | 1.04 | 477 856 | 5.2 % | 0.05 | 2 030 890 | 22 % | 0.23 | 6 649 878 | 72 % | 0.75 | 40 308 | 0.4 % | 0.00 |
| 11 | 6.2 | 3.77 | 0.40 | NA | | | NA | | | NA | | | 3 766 686 | 100 % | 0.40 |
| 12 | 9.0 | 3.46 | 0.54 | NA | | | NA | | | NA | | | 70 208 | 2.0 % | 0.01 |
| 13 | 6.0 | 6.58 | 1.24 | 5 384 185 | 81.8 % | 1.02 | NA | | | NA | | | 50 904 | 0.8 % | 0.01 |
| 14 | 9.3 | 42.47 | 2.57 | 4 351 435 | 10.2 % | 0.26 | 4 457 867 | 10 % | 0.27 | 33 576 647 | 79 % | 2.03 | 81 020 | 0.2 % | 0.00 |
| 15 | 6.9 | 2.16 | 0.44 | NA | | | NA | | | NA | | | 274 169 | 12.7 % | 0.06 |
| 16 | 8.7 | 4.66 | 0.65 | NA | | | NA | | | NA | | | 55 787 | 1.2 % | 0.01 |
| 17 | 4.0 | 0.23 | 0.31 | NA | | | NA | | | NA | | | 226 180 | 100 % | 0.31 |
| 18 | 12.9 | 11.90 | 1.44 | 5 306 385 | 44.6 % | 0.64 | 3 297 800 | 28 % | 0.40 | 3 038 516 | 26 % | 0.37 | 255 746 | 2.1 % | 0.03 |
| 20 | 12.9 | 11.02 | 1.19 | 574 218 | 5.2 % | 0.06 | 3 232 352 | 29 % | 0.35 | 6 552 703 | 59 % | 0.71 | 0 | 0.0 % | 0.00 |
| 21 | 13.1 | 842.09 | 149.65 | 497 281 | 0.1 % | 0.09 | 9 447 040 | 1 % | 1.68 | 831 672 535 | 99 % | 147.80 | 474 469 | 0.1 % | 0.08 |
| 22 | 7.2 | 8.62 | 1.00 | NA | | | NA | | | NA | | | 0 | 0.0 % | 0.00 |
| 23 | 8.4 | 17.97 | NA | NA | | | NA | | | NA | | | 12 881 | 0.1 % | NA |
| 24 | 4.9 | 266.18 | 30.76 | NA | | | NA | | | NA | | | 435 714 | 0.2 % | 0.05 |
| 25 | 9.7 | 1.40 | 0.39 | 547 000 | 39.0 % | 0.15 | NA | | | 653 000 | 47 % | 0.18 | 547 000 | 39.0 % | 0.15 |
| 26 | 10.8 | 7.19 | 0.71 | 623 664 | 8.7 % | 0.06 | 3 162 240 | 44 % | 0.31 | 3 408 192 | 47 % | 0.33 | 7 194 096 | 100 % | 0.71 |
| 27 | 10.8 | 388.84 | 20.30 | 11 028 626 | 2.8 % | 0.58 | NA | | | 377 541 509 | 97 % | 19.71 | 11 294 307 | 2.9 % | 0.59 |
| 28 | 9.4 | 7.38 | 0.52 | NA | | | 3 510 671 | 48 % | 0.25 | 3 722 846 | 50 % | 0.26 | 0 | 0.0 % | 0.00 |
| 29 | 9.4 | 2.89 | 0.76 | NA | | | NA | | | NA | | | 67 035 | 2.3 % | 0.02 |
| 30 | 6.3 | 5.54 | 0.53 | 1 358 440 | 24.5 % | 0.13 | 1 824 770 | 33 % | 0.17 | 2 274 000 | 41 % | 0.22 | 82 580 | 1.5 % | 0.01 |
| 31 | 6.7 | 8.35 | 0.69 | 2 595 498 | 31.1 % | 0.21 | 3 604 606 | 43 % | 0.30 | 2 144 738 | 26 % | 0.18 | 281 000 | 3.4 % | 0.02 |
| 32 | 11.4 | 3.51 | 0.60 | 799 098 | 22.8 % | 0.14 | 1 158 205 | 33 % | 0.20 | 1 509 710 | 43 % | 0.26 | 0 | 0.0 % | 0.00 |
| 33 | 4.6 | 2.56 | 0.55 | NA | | | NA | | | NA | | | 1 465 000 | 57.3 % | 0.32 |
| 34 | 8.6 | 6.90 | 0.66 | NA | | | 441 049 | 6 % | 0.04 | NA | | | 6 902 700 | 100 % | 0.66 |
| 35 | 5.7 | 2.15 | 0.59 | NA | | | 451 435 | 21 % | 0.12 | 600 219 | 28 % | 0.17 | 551 648 | 25.6 % | 0.15 |

| Site label | Nelson Index | Total water consumed | Specific water consumption | Water for industrial processes | | | Water for boilers feed | | | Water for cooling systems | | | Proportion of use of fresh water | | |
|--------------------------|--------------|----------------------|----------------------------|--------------------------------|---------------|-------------------|------------------------|-------------|-------------------|---------------------------|-------------|-------------------|----------------------------------|---------------|-------------------|
| | | Mm ³ /yr | m ³ /t | m ³ /yr | % | m ³ /t | m ³ /yr | % | m ³ /t | m ³ /yr | % | m ³ /t | m ³ /yr | % | m ³ /t |
| 37 | 9.5 | 7.14 | 0.98 | 1952263 | 27.3 % | 0.27 | 1760370 | 25 % | 0.24 | 3415251 | 48 % | 0.47 | 4799449 | 67.2 % | 0.66 |
| 38 | 7.3 | 3.46 | 0.42 | 17000 | 0.5 % | 0.002 | NA | | | NA | | | 142000 | 4.1 % | 0.02 |
| 39 | 8.2 | 1.75 | 0.17 | NA | | | NA | | | NA | | | 0 | 0.0 % | 0.00 |
| 40 | 6.2 | 0.72 | 0.13 | NA | | | NA | | | NA | | | 721000 | 100 % | 0.13 |
| 41 | 6.5 | 12.41 | 3.15 | NA | | | NA | | | NA | | | 1171395 | 9.4 % | 0.30 |
| 42 | 12.0 | 5.41 | 0.50 | NA | | | NA | | | NA | | | 125681 | 2.3 % | 0.01 |
| 43 | 8.7 | 148.39 | 9.59 | NA | | | 8201500 | 6 % | 0.53 | NA | | | 450000 | 0.3 % | 0.03 |
| 44 | 1.6 | 0.85 | 0.19 | NA | | | NA | | | NA | | | 14100 | 1.6 % | 0.00 |
| 45 | 8.4 | 24.87 | 2.47 | 530000 | 2.1 % | 0.05 | 4016000 | 16 % | 0.40 | 20260000 | 81 % | 2.02 | 35000 | 0.1 % | 0.00 |
| 46 | 6.2 | 2.69 | 0.28 | 252957 | 9.4 % | 0.03 | 2200270 | 82 % | 0.23 | 175800 | 7 % | 0.02 | 59697 | 2.2 % | 0.01 |
| 47 | 11.6 | 5.52 | 0.46 | 431427 | 7.8 % | 0.04 | 4076298 | 74 % | 0.34 | 748275 | 14 % | 0.06 | 262800 | 4.8 % | 0.02 |
| 48 | 8.4 | 14.85 | 2.15 | 3861846 | 26.0 % | 0.56 | 4214512 | 28 % | 0.61 | 6140076 | 41 % | 0.89 | 8713325 | 58.7 % | 1.26 |
| 49 | 5.7 | 3.70 | 0.25 | 1795317 | 48.5 % | 0.12 | 1909028 | 52 % | 0.13 | NA | | | 3704345 | 100 % | 0.25 |
| 50 | 10.5 | 3.10 | 0.67 | 859919 | 27.7 % | 0.19 | 984095 | 32 % | 0.21 | 934425 | 30 % | 0.20 | 0 | 0.0 % | 0.00 |
| 51 | 8.4 | 4.50 | 1.02 | 1402658 | 31.2 % | 0.32 | 1837388 | 41 % | 0.42 | 1074965 | 24 % | 0.24 | 2337675 | 52.0 % | 0.53 |
| 52 | 10.9 | 1.48 | 0.30 | NA | | | NA | | | NA | | | 34124 | 2.3 % | 0.01 |
| 53 | 3.8 | 0.96 | NA | 557000 | 58.2 % | NA | 400000 | 42 % | NA | NA | | | 450000 | 47.0 % | NA |
| 56 | 12.4 | 2.70 | 0.43 | 680236 | 25.2 % | 0.11 | 768017 | 28 % | 0.12 | 928026 | 34 % | 0.15 | 0 | 0.0 % | 0.00 |
| 57 | 8.2 | 68.84 | 11.91 | 3109536 | 4.5 % | 0.54 | 2073024 | 3 % | 0.36 | 63572370 | 92 % | 11.00 | 84802 | 0.1 % | 0.01 |
| 58 | 10.2 | 12.15 | 1.06 | NA | | | 3613982 | 30 % | 0.32 | 8284316 | 68 % | 0.72 | 248923 | 2.0 % | 0.02 |
| Number of values: | 57 | 53 | 51 | 31 | 31 | 30 | 31 | 31 | 30 | 30 | 30 | 30 | 52 | 52 | 50 |
| Minimum: | | 0.23 | 0.13 | 15000 | 0.06 % | 0.002 | 360000 | 1 % | 0.04 | 54000 | 7 % | 0.02 | 0 | 0.0 % | 0.00 |
| Maximum: | | 842 | 149.65 | 11028626 | 81.8 % | 1.02 | 9447040 | 83 % | 1.68 | 831672535 | 99 % | 147.80 | 11294307 | 100 % | 1.26 |
| Average: | | 39 | 5.89 | 1681185 | 19.7 % | 0.22 | 2462633 | 32 % | 0.33 | 47760617 | 51 % | 7.69 | 1140267 | 23.3 % | 0.16 |
| 5th percentile | | 0.73 | 0.18 | 24000 | 0.36 % | 0.013 | 391546 | 2 % | 0.110 | 109360 | 9 % | 0.019 | 0 | 0.0 % | 0.000 |
| 95th percentile | | 196 | 25.53 | 5345285 | 53.3 % | 0.612 | 6329684 | 78 % | 0.603 | 236255396 | 97 % | 28.97 | 7033828 | 100 % | 0.659 |

NA: these data have not been made available to the TWG.
Source: [TWG data collection questionnaires]

Figure 3.6 shows in more detail, and with a linear scale instead of the logarithmic one used in Figure 3.5, a breakdown of the main water usages for the subsample of European refineries for which this information was fully available. What appears is the rather constant water use related to the boiler feed in all of these sites, regardless of their increasing total site usage. Furthermore, this figure clearly displays the beneficial effect of the closed-loop cooling system on the site's overall specific usage.

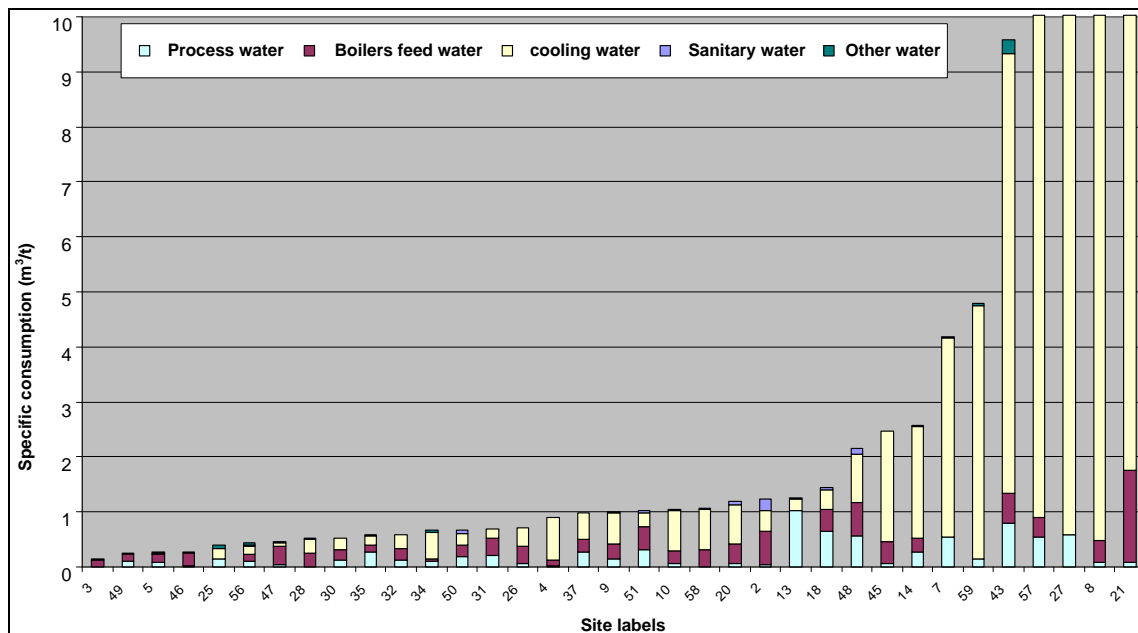


Figure 3.6: Specific water consumption breakdown for a sample of European refineries

3.1.2 Emissions to air

The main air emissions from a refinery are CO₂, SO_x, NO_x, VOC and particulates (dust, soot and associated heavy metals (mainly V and Ni)). However, noise, odour, H₂S, NH₃, CO, CS₂, benzene, toluene, dioxins, HF and HCl also contribute to the air emissions. They emerge typically from sources such as stacks of process furnaces and boilers, regenerators (FCC), individual items such as valves and pump seals, and to a lesser extent from flares and incinerator stacks. Some documents establish emissions factors for the calculation of air emissions from refineries. [181, USAEPA 1996], [172, MRI 1997] The E-PRTR regulation [74, EEA 2010] requires refineries to make inventories and report annual emissions of a large number of substances since 2007.

3.1.2.1 Carbon dioxide emissions

Almost all of the carbon present in crude oil, once produced from the oil well, will be converted into CO₂. A small portion (<3 – 10 %) of the CO₂ will be converted in the refinery during the processing of crude oil into marketable products. The remainder will be converted into CO₂ once the refined oil products are sold and subsequently consumed by the various sectors of industry and private consumers.

In 2007, oil refineries in the EU-27 (Romania and Bulgaria excluded) emitted around 135 Mt of CO₂. In 1990, this figure was 115 Mt of CO₂. The 15 % increase of CO₂ emissions between 1990 and 2007 is mainly linked to the increasing average site complexity, the diversification of refining processes and the significant increase of hydrotreatment capacities for deeper product desulphurisation and conversion.

The share of CO₂ emissions from oil refining in the total greenhouse gas emissions was, in 2007, around 3 % at the EU-15 level. At the individual Member State level, it ranged from around 0.5 % (for Ireland) to 5 % (for the Netherlands).

Actual specific emissions of a sample of European refineries for recent years are displayed in Table 3.2 in Section 3.1.1.1. The largest part (90 % of them from the 5th to 95th percentiles) range within 0.11 – 0.39 t/t of feedstock processed, with an average of 0.22 t/t. As shown in Figure 3.3, the highest values are often associated with the most complex sites.

At the individual site level, CO₂ emissions by themselves ranged from 0.168 to 5.547 million tonnes per year. However, the lowest and highest emissions originate from two refineries with nearly the same CO₂ specific emissions (0.28 – 0.29 t/t), which is close to the European average.

The main emission sources for CO₂ are the process furnaces and boilers, gas turbines, FCC regenerators, flare systems and incinerators.

3.1.2.2 Nitrogen oxides emissions

The term NO_x, by convention, only refers to NO (nitrogen monoxide) and NO₂ (nitrogen dioxide). N₂O can be also found in flue-gases from FCCs and some SCR. In most combustion processes NO contributes to over 90 % of the total NO_x. However, as it is rapidly oxidised to NO₂ in the atmosphere, emissions of NO are expressed as NO₂.

Contributing processes and units

Based on the information gathered by the TWG, Figure 3.7 and Figure 3.8 display site-level data on the NO_x specific emissions and the main NO_x-contributing units and processes within a sample of European refineries. The main emission sources of NO_x are combustion processes, i.e. process furnaces and boilers, CHP and gas turbines, FCC regenerators, and to a lesser extent, eventual waste gas incinerators and the flare system. However, the respective weights of these units in the overall site emissions are highly variable, as shown in the same figures.

In the case of refineries without a FCC unit, the major NO_x contribution obviously comes from furnaces and boilers, which account most often for about 60 – 90 % of emissions, as shown in Figure 3.7. Gas turbines and CHP, when they are operated on such plants, are responsible for a significant part (30 – 50 %) of NO_x emissions, and are associated with the highest specific emissions at the site level. SRU and flare systems usually account for less than 5 – 10 % of emissions.

In the case of a refinery configuration including a FCC unit, furnaces and boilers remain the major NO_x contributors and generate 50 – 80 % of site emissions, while the FCC by itself may only represent 15 – 25 % of them. As displayed in Figure 3.8, most of the remainder is emitted by CHP and gas turbines which, as stated above, are clearly related to highest specific emissions reported.

When operating a coker, coking emissions can also represent a very significant contribution (up to 40 %) which appears here in the ‘Other’ category.

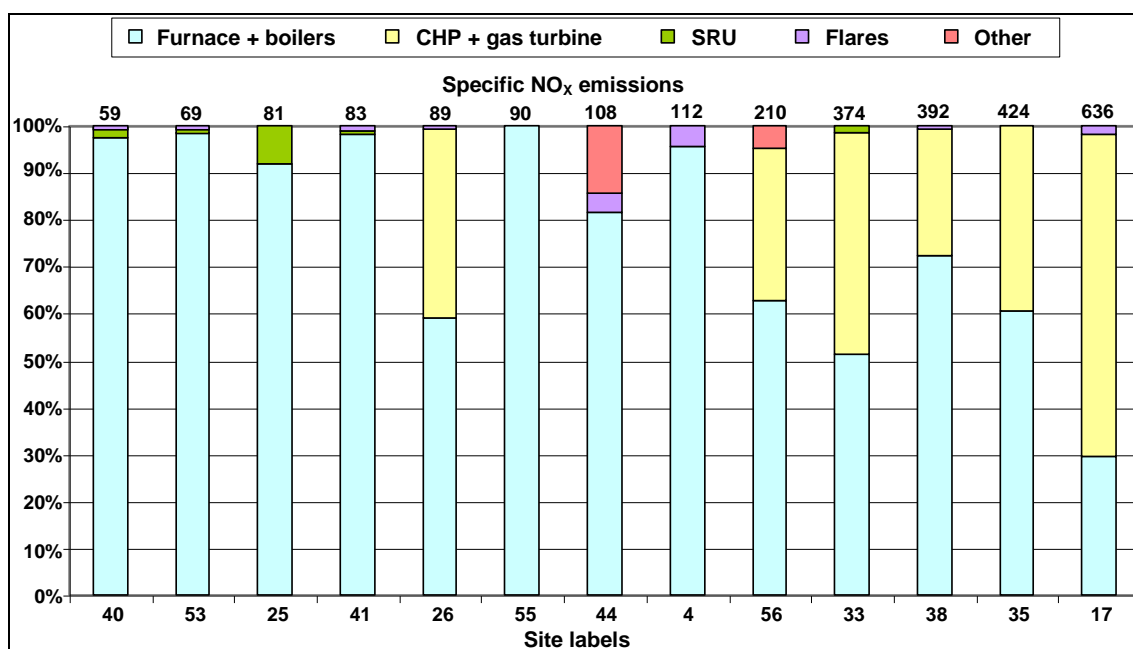


Figure 3.7: Respective weights of the main NO_x-contributing processes for 12 European refineries not operating a FCC unit as a function of their specific emissions (g/t of feed)

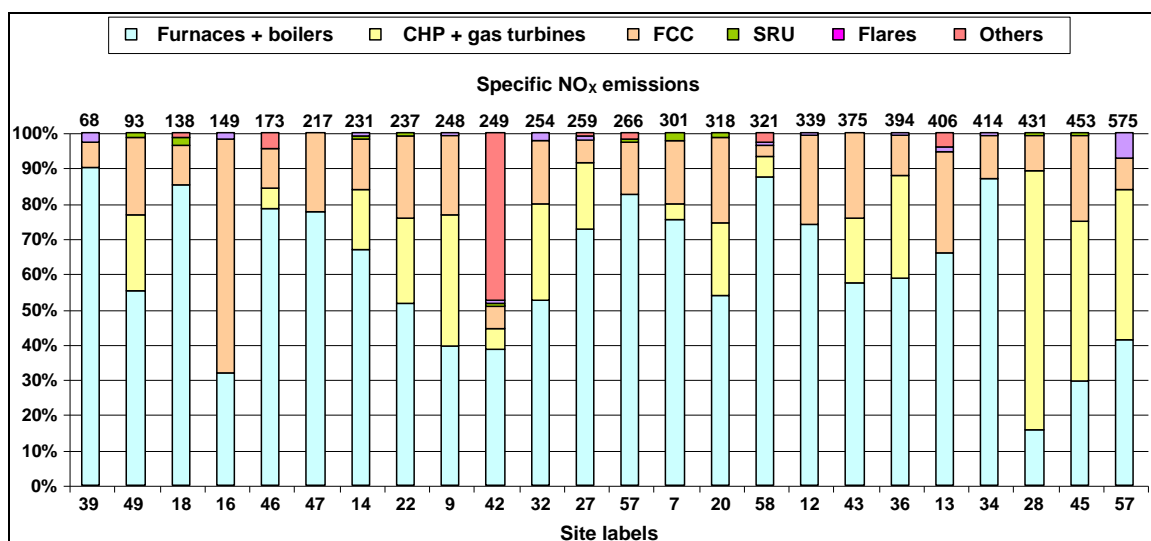


Figure 3.8: Respective weights of the main NO_x-contributing processes for 24 European refineries operating a FCC unit as a function of their specific emissions (g/t of feed)

Influence of the overall site configuration on NO_x emissions

The range of NO_x emissions reported for the site sample displayed in Figure 3.9 within the period 2007 – 2008 is approximately 100 – 6 000 tonnes per year. The specific emission range of NO_x varies from 68 to 575 tonnes of NO_x per million tonnes of crude oil processed, with most of these refineries (80 % of data – from the 10th to 90th percentiles) emitting within the range of 100 – 450 g/t. The average specific emissions achieved within the particular subgroup of refineries without a FCC is 258 g/t processed. This average only increases to up to 269 g/t processed (+4 %) for the subgroup operating a FCC. Therefore, FCC configurations should not be considered to noticeably increase NO_x emissions at the site level.

Figure 3.9 displays the distribution of the Nelson Index and the specific energy consumption for these two subgroups of European refineries, each of them ordered by ascending specific NO_x emission. No obvious correlation can be seen as far as the Nelson Index is concerned, and the

specific NO_x emissions of non-FCC sites and FCC sites evolve basically in the same range of 60 – 600 g/t of feedstock processed. And, for both categories of refineries, the highest specific NO_x emissions are clearly associated with the highest specific energy consumption.

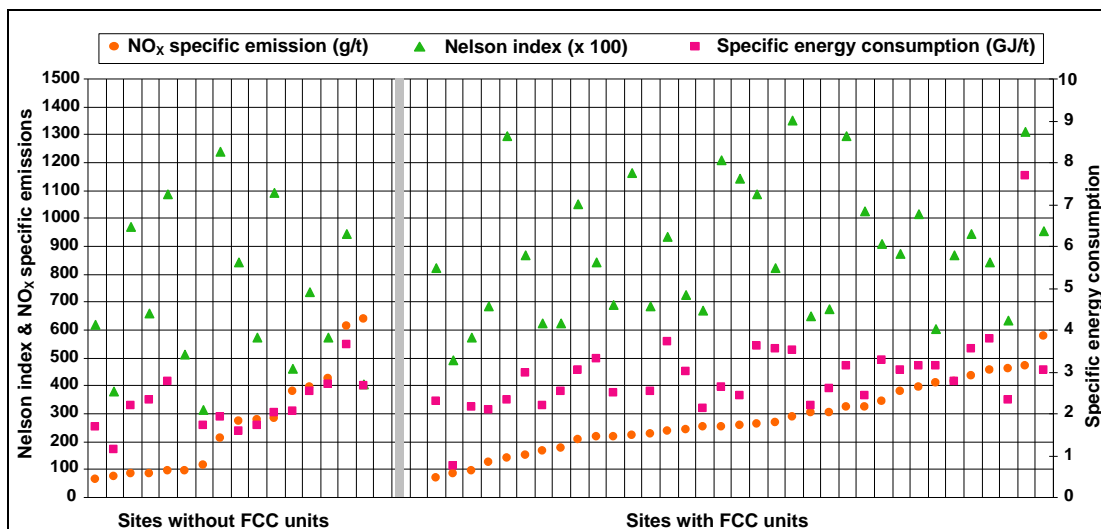


Figure 3.9: Influence of the configuration, complexity and specific energy consumption on NO_x emissions

Influence of the refinery fuel mix on NO_x emissions

NO_x emissions from refineries depend on the fuel type (nitrogen or hydrogen content of fuel), combustor equipment design, NO_x control system, and operating conditions. In the particular case of FCC regenerator flue-gas, NO_x emissions are, in general, not thermal NO_x produced by the interference of air-contained nitrogen in high-temperature combustion, but are directly linked to the nitrogen content in the feedstock. Accordingly, large differences in the NO_x emission levels can be expected between refineries and even between different combustion installations at the same refinery at different times. Nevertheless, general trends can be observed showing a rather clear correlation between NO_x emissions and the use of gaseous fuels for energy system firing: as shown in Figure 3.10, the highest values of NO_x specific emissions recorded within a sample of 51 European refineries are associated with the lowest percentages of energy coming from gaseous fuels in the fuel mix used at these sites (regardless of the part taken by the eventual natural gas external supply in these gaseous fuels).

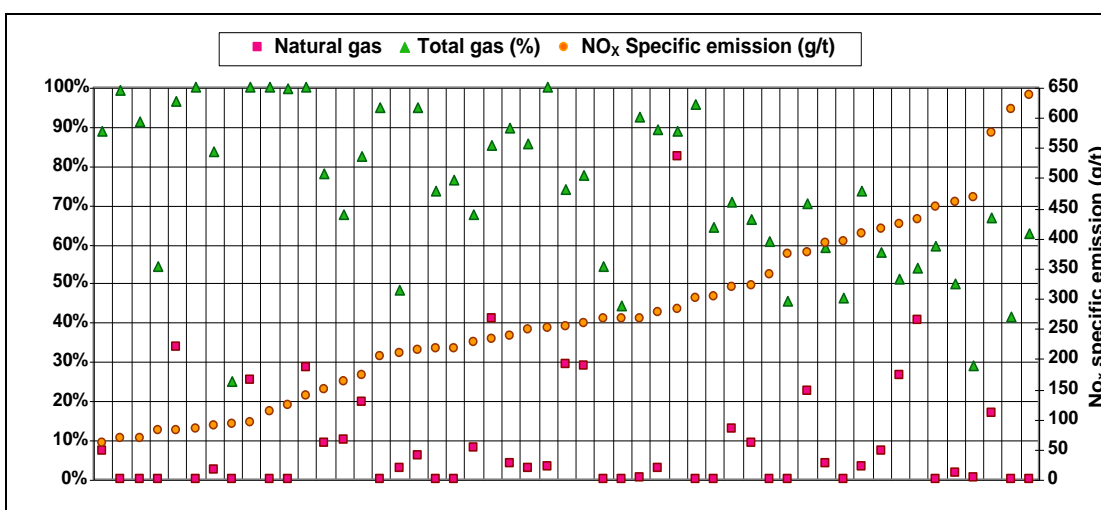


Figure 3.10: Influence of the gaseous fuels used for energy supply on the site NO_x emissions

Table 3.4: NO_x emissions and main contributing unit data for 58 European refineries

| Questionnaire | Nelson Index | FCC? (yes=1) | Year | Total NO _x | | NO _x specific emission | | Furnace + boilers | | CHP + stand-alone gas turbines | | FCC | | SRU | | Flares | | Others | |
|---------------|--------------|--------------|------|-----------------------|-------------------------|-----------------------------------|-------|-------------------|------|--------------------------------|------|------|-------|-------|-------|--------|--------|--------|---|
| | | | | t/yr | g/t | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % |
| 40 | 6.2 | 0 | 2008 | 337 | 59 | 328 | 97 % | - | - | - | - | 7.7 | 2.3 % | 0.8 | 0.2 % | 0 | - | | |
| 53 | 3.8 | 0 | 2008 | 380 | 69⁽¹⁾ | 375 | 99 % | - | - | - | - | 3 | 0.8 % | 2 | 0.5 % | 0 | - | | |
| 25 | 9.7 | 0 | 2007 | 294 | 81 | 270 | 92 % | - | - | - | - | 24.2 | 8.2 % | NA | - | 0 | - | | |
| 41 | 6.5 | 0 | 2008 | 329 | 83 | 323 | 98 % | - | - | - | - | 2 | 0.6 % | 4 | 1.2 % | 0 | - | | |
| 26 | 10.8 | 0 | 2008 | 910 | 89 | 536 | 59 % | 366 | 40 % | - | - | 1.66 | 0.2 % | 5.75 | 0.6 % | 0 | - | | |
| 55 | 5.1 | 0 | 2008 | 85 | 90 | 85 | 100 % | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 44 | 1.6 | 0 | 2007 | 476 | 108 | 389 | 82 % | - | - | - | - | 0 | - | 18 | 3.8 % | 69 | 14.5 % | | |
| 4 | 3.1 | 0 | 2008 | 548 | 112 | 523 | 95 % | - | - | - | - | 0 | - | 25 | 4.6 % | 0 | - | | |
| 56 | 12.4 | 0 | 2008 | 1317 | 210 | 824 | 63 % | 431 | 33 % | - | - | 0 | - | NA | - | 61 | 4.6 % | | |
| 19 | 5.1 | 0 | 2008 | 773 | 230 | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 48 | 8.4 | 0 | 2007 | 1842 | 267 | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 3 | 5.7 | 0 | 2006 | 931 | 267 | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 2 | 11.2 | 0 | 2007 | 165 | 272 | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 52 | 10.9 | 0 | 2008 | 1384 | 277 | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 33 | 4.6 | 0 | 2008 | 1725 | 374 | 887 | 51 % | 814 | 47 % | - | - | 24 | 1.4 % | NA | - | 0 | - | | |
| 38 | 7.3 | 0 | 2008 | 3208 | 392 | 2316 | 72 % | 870 | 27 % | - | - | 0 | - | 22 | 0.7 % | 0 | - | | |
| 35 | 5.7 | 0 | 2008 | 1535 | 424 | 927 | 60 % | 609 | 40 % | - | - | 0 | - | NA | - | 0 | - | | |
| 8 | NA | 0 | 2008 | 477 | 500 | 476 | 100 % | - | - | - | - | - | - | NA | - | 0 | - | | |
| 29 | 9.4 | 0 | 2007 | 2337 | 612 | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 17 | 4.0 | 0 | 2008 | 463 | 636 | 136 | 29 % | 318 | 69 % | - | - | - | - | 9 | 1.9 % | 0 | - | | |
| 23 | 8.4 | 0 | 2007 | 1030 | (²) | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 39 | 8.2 | 1 | 2008 | 687 | 68 | 620 | 90 % | - | - | 48 | 7 % | 0 | - | 19 | 2.8 % | 0 | - | | |
| 24 | 4.9 | 1 | 2007 | 694 | 80 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 49 | 5.7 | 1 | 2008 | 1400 | 93 | 760 | 54 % | 300 | 21 % | 300 | 21 % | 20 | 1.4 % | NA | - | 0 | - | | |
| 5 | 6.8 | 1 | 2008 | 343 | 124 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 1 | 6.2 | 1 | 2008 | 1203 | 132 | NA | - | 564 | 47 % | 53 | 4 % | NA | - | NA | - | NA | - | | |
| 18 | 12.9 | 1 | 2007 | 1144 | 138 | 959 | 84 % | - | - | 127 | 11 % | 20.7 | 1.8 % | NA | - | 17.65 | 1.5 % | | |
| 16 | 8.7 | 1 | 2008 | 1064 | 149 | 340 | 32 % | - | - | 702 | 66 % | 0 | - | 21.28 | 2.0 % | 0 | - | | |
| 11 | 6.2 | 1 | 2008 | 1512 | 162 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 46 | 6.2 | 1 | 2008 | 1685 | 173 | 1322 | 78 % | 101 | 6 % | 187 | 11 % | - | - | NA | - | 75 | 4.5 % | | |
| 54 | 5.4 | 1 | 2007 | 1930 | 179 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 50 | 10.5 | 1 | 2008 | 944 | 204 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 51 | 8.4 | 1 | 2007 | 939 | 213 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 15 | 6.9 | 1 | 2007 | 1049 | 216 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 47 | 11.6 | 1 | 2008 | 2577 | 217 | 2002 | 78 % | - | - | 575 | 22 % | - | - | NA | - | 0 | - | | |
| 10 | 6.8 | 1 | 2007 | 2002 | 226 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 14 | 9.3 | 1 | 2008 | 3831 | 231 | 2554 | 67 % | 661 | 17 % | 540 | 14 % | 34 | 0.9 % | 42 | 1.1 % | 0 | - | | |
| 22 | 7.2 | 1 | 2007 | 2047 | 237 | 1052 | 51 % | 498 | 24 % | 481 | 23 % | 17.4 | 0.8 % | NA | - | 0 | - | | |
| 9 | 6.6 | 1 | 2008 | 1418 | 248 | 557 | 39 % | 532 | 38 % | 324 | 23 % | 0 | 0.0 % | 4.9 | 0.3 % | 0 | - | | |
| 42 | 12.0 | 1 | 2008 | 2723 | 249 | 1056 | 39 % | 154 | 6 % | 178 | 7 % | 21 | 0.8 % | 21 | 0.8 % | 1293 | 47.5 % | | |
| 32 | 11.4 | 1 | 2008 | 1494 | 254 | 783 | 52 % | 410 | 27 % | 265 | 18 % | - | 0.0 % | 36 | 2.4 % | 0 | - | | |
| 27 | 10.8 | 1 | 2006 | 4959 | 259 | 3608 | 73 % | 920 | 19 % | 357 | 7 % | 14 | 0.3 % | 16 | 0.3 % | 44 | 0.9 % | | |
| 57 | 8.2 | 1 | 2008 | 1535 | 266 | 1261 | 82 % | - | - | 229 | 15 % | 13 | 0.8 % | 0.8 | 0.1 % | 28 | 1.8 % | | |
| 6 | 13.5 | 1 | 2008 | 3508 | 283 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 7 | 6.4 | 1 | 2008 | 984 | 301 | 742 | 75 % | 43 | 4 % | 177 | 18 % | 22 | 2.2 % | NA | - | 0 | - | | |
| 31 | 6.7 | 1 | 2008 | 3654 | 302 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 20 | 12.9 | 1 | 2007 | 2942 | 318 | 1589 | 54 % | 607 | 21 % | 706 | 24 % | 40 | 1.4 % | NA | - | 0 | - | | |
| 58 | 10.2 | 1 | 2008 | 3667 | 321 | 3201 | 87 % | 218 | 6 % | 122 | 3 % | - | - | 29 | 0.8 % | 98 | 2.7 % | | |

| Questionnaire | Nelson Index | FCC? (yes=1) | Year | Total NO _x | | Furnace + boilers | | CHP + stand-alone gas turbines | | FCC | | SRU | | Flares | | Others | |
|--------------------------|--------------|--------------|------|-----------------------|------------|-------------------|-------|--------------------------------|------|-------|------|------|--------|--------|-------|--------|--------|
| | | | | t/yr | g/t | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % |
| 12 | 9.0 | 1 | 2008 | 2175 | 339 | 1608 | 74 % | - | - | 561 | 26 % | - | - | NA | - | 5.89 | 0.3 % |
| 43 | 8.7 | 1 | 2008 | 5803 | 375 | 3339 | 58 % | 1068 | 18 % | 1396 | 24 % | 0 | 0.0 % | NA | - | 0 | - |
| 36 | 10.1 | 1 | 2008 | 2213 | 394 | 1304 | 59 % | 644 | 29 % | 252 | 11 % | 0 | 0.0 % | 14 | 0.6 % | 0 | - |
| 13 | 6.0 | 1 | 2008 | 2155 | 406 | 1419 | 66 % | - | - | 618 | 29 % | NA | - | 27.6 | 1.3 % | 89 | 4.1 % |
| 34 | 8.6 | 1 | 2007 | 4333 | 414 | 3785 | 87 % | - | - | 542 | 13 % | NA | - | 22.27 | 0.5 % | 0 | - |
| 28 | 9.4 | 1 | 2008 | 6147 | 431 | 968 | 16 % | 4523 | 74 % | 626 | 10 % | 30 | 0.5 % | - | - | 0 | - |
| 45 | 8.4 | 1 | 2008 | 4550 | 453 | 1340 | 29 % | 2080 | 46 % | 1125 | 25 % | 10 | 0.2 % | 4 | 0.1 % | 0 | - |
| 30 | 6.3 | 1 | 2007 | 4826 | 460 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - |
| 21 | 13.1 | 1 | 2007 | 2634 | 468 | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - |
| 37 | 9.5 | 1 | 2008 | 4197 | 575 | 1728 | 41 % | 1792 | 43 % | 381 | 9 % | 1.2 | 0.03 % | 294.2 | 7.0 % | 0 | - |
| Number of values: | | 58 | 58 | 58 | 57 | 38 | 34 | 24 | 24 | 25 | 25 | 21 | 21 | 22 | 22 | 10 | 10 |
| Sum (kt): | | - | - | 111.5 | - | 46292 | - | 18523 | - | 10873 | - | 306 | - | 639 | - | 1781 | - |
| Minimum: | | - | - | 85 | 59 | 85 | 16 % | 0 | 0 % | 48 | 3 % | 0 | 0 % | 0.8 | 0.1 % | 6 | 0.3 % |
| 5th Percentile: | | - | - | 369 | 78 | 250 | 29 % | 52 | 5 % | 67 | 5 % | 0 | 0.0 % | 0.9 | 0.2 % | 11 | 0.5 % |
| 50th Percentile: | | - | - | 1923 | 249 | 943 | 69 % | 548 | 27 % | 357 | 15 % | 14 | 0.8 % | 19 | 0.8 % | 65 | 3.4 % |
| 95th Percentile: | | - | - | 4238 | 515 | 3379 | 99 % | 2037 | 65 % | 1041 | 28 % | 34 | 2.3 % | 42 | 4.5 % | 755 | 32.6 % |
| Maximum: | | - | - | 6147 | 636 | 3785 | 100 % | 4523 | 74 % | 1396 | 66 % | 40 | 8 % | 294 | 7 % | 1293 | 47 % |

(¹) Based on 90 % of the production capacity.
(²) The annual feedstock refined has not been made available to the TWG.
NA These data have not been made available to the TWG.
(-) Not applicable.
Source: TWG data collection questionnaires

3.1.2.3 Particulate emissions

The concern with particulate emissions (including heavy metals) stems from health effects. The main emission sources are process furnaces/boilers (mainly those fired with (liquid) heavy fuel oil), catalytic cracker regenerators, coke plants, incinerators, decoking and soot blowing of furnaces and flares. As shown, the range of emissions found in most European refineries (5th to 95th percentiles within a sample of 43 plants) is approximately from 20 to 700 tonnes of particulates emitted per year, which corresponds to a specific emission range from 4 to 75 tonnes of particulates per million tonnes of crude oil processed. The lower emission value can be achieved in refineries burning substantial amounts of gas or when effective dedusting devices (e.g. ESP) are used.

Table 3.5: Specific emission ranges of PM, PM₁₀ and PM_{2.5} for 43 European refineries

| Type of particulates | Unit | Specific load | | No |
|-------------------------|------|-----------------------|-----------------|----|
| | | 5th – 95th percentile | 50th percentile | |
| PM (total) | g/t | 4 – 75 | 181 | 43 |
| PM₁₀ | g/t | 0.1 – 45 | 15 | 25 |
| PM_{2.5} | g/t | 0.01 – 12 | 4 | 4 |

Important heavy metals in crude oils are arsenic, mercury, nickel and vanadium. Nickel and vanadium are enriched in the residues during distillation (see Table 3.55 in Section 3.10.2) and are removed with the particulate matter by ESP or fabric filters after combustion in the furnaces

or after the regeneration of catalysts by burning off. Data on metal emissions collected from a sample of European refineries are available in Table 3.12.

3.1.2.4 Sulphur oxides emissions

Sulphur emissions to the atmosphere have long been an issue for refineries. All crude oils contain sulphur compounds. Consequently, when firing non- or partially desulphurised refinery fuels, SO_2 and SO_3 are emitted. There is a direct relation between the sulphur content of the fuel and the amount of SO_x emitted (for example, a fuel with 1 % sulphur generates a flue-gas with around 1700 mg/Nm^3 of SO_x). The sulphur, which is not extracted from the products in the refinery, will remain in the various products and will be burnt to SO_x by the various end-users. The refinery, as a consumer of fuel for its energy use, similarly emits SO_x . However, natural gas, as a growing external energy supply in oil refining, normally contains only traces of sulphur compounds.

Sulphur input/output mass balance

The sulphur output distribution can vary greatly depending on FCC unit, furnace and boiler operation modes, SRU and hydrotreater performances and the overall share of products not for combustion.

According to a 2006 investigation by CONCAWE based on 67 European refineries (accounting for 68 % of the crude and intermediate feedstock refined in the OECD), 156 kt of sulphur have been emitted to air (i.e. 312 kt of SO_2 after oxidation) out of a 4 183 kt total sulphur intake, representing 3.73 % of sulphur emitted and 45.1 % of sulphur recovered, as shown in Figure 3.11. A similar survey based on 2010 data from 61 refineries shows an increase in the percentage of the recovered sulphur to 55.4 %.

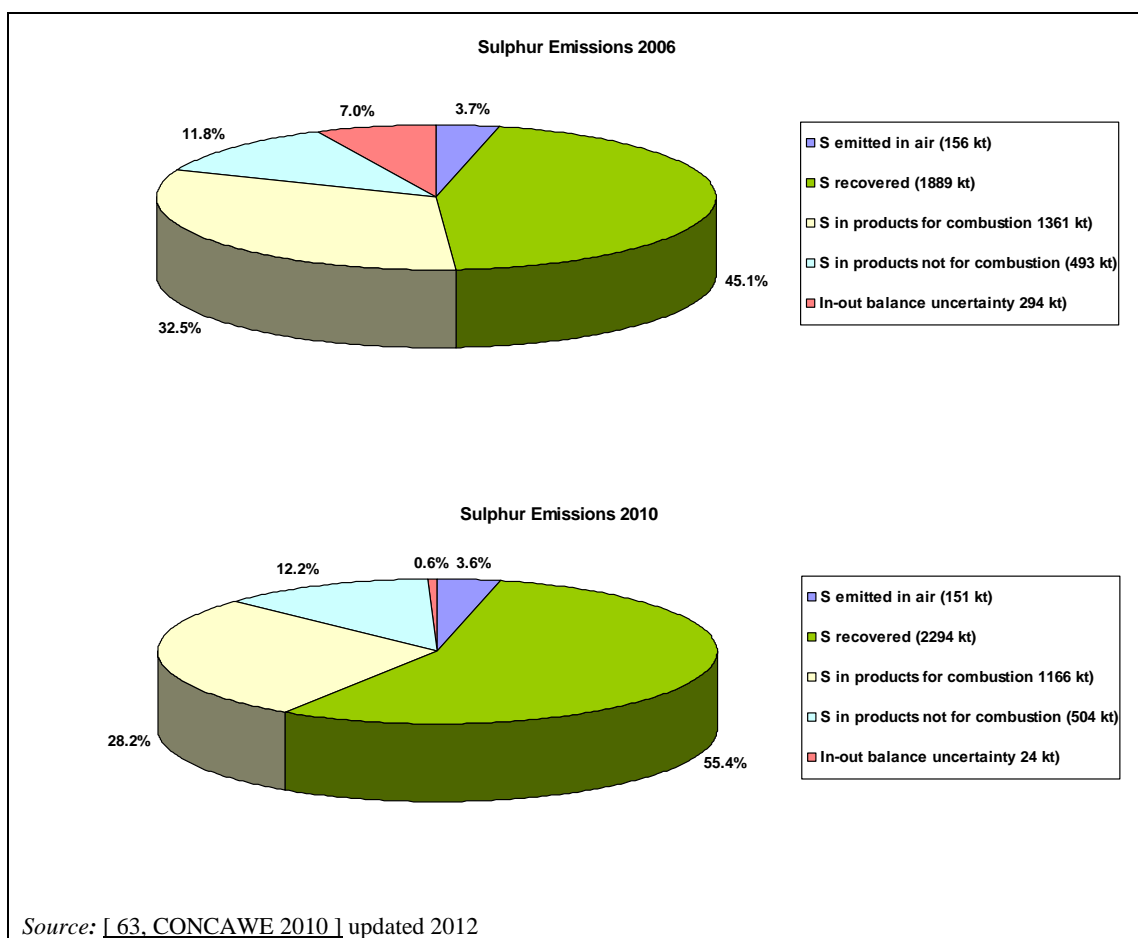


Figure 3.11: Average sulphur output distribution from a sample of European refineries

Moreover, based on the information gathered by the TWG, Table 3.6 displays site-level data on the sulphur input, specific emissions and the fuels used in a set of 49 European refineries. Within this sample, the median percentage of sulphur emitted in the air is 4.4 % and the median percentage of sulphur recovered by the SRUs is 44.7 % of the refinery sulphur input (see Section 3.23.2 on emissions from SRU). These two values are very close to the ratios displayed in Figure 3.11. It means that this European sample is representative of the European global situation as reflected in the CONCAWE survey.

Table 3.6: Sulphur balance and specific emissions to air for a sample of 49 European refineries

| Questionnaire (1) | Specific SO ₂ (g/t crude treated) (2) | Sulphur in crude (%) | Sulphur in intermediate products (%) | Sulphur input in feedstock (t) (3) | Sulphur input in external fuels (t) | Total Sulphur input (t) | Sulphur in RFG (ppm) | Sulphur in liquid fuel (%) | RFG/total fuel burnt (%) | Natural gas/Total fuel burnt (%) | Total gas/Total fuel burnt (%) | Sulphur emitted in air/input (%) |
|-------------------|--|----------------------|--------------------------------------|------------------------------------|-------------------------------------|-------------------------|----------------------|----------------------------|--------------------------|----------------------------------|--------------------------------|----------------------------------|
| 41 | 12 | 0.22 | - | 8672 | 0 | 8672 | 15 | 0.68 | 100 | 0 | 100 | 0.3 |
| 40 | 29 | 0.24 | NA | 12984 | 0 | 12984 | 19 | 0.40 | 82 | 7 | 89 | 0.6 |
| 39 | 34 | 1.10 | NA | 106458 | 0 | 106458 | 24 | 0.002 | 99 | 0 | 99 | 0.2 |
| 4 | 79 | 0.50 | - | 24500 | 0 | 24500 | 100 | - | 100 | 0 | 100 | 0.8 |
| 18 | 161 | 1.22 | 0.05 | 86856 | 0 | 86857 | 647 | 0.09 | 72 | 28 | 100 | 0.8 |
| 25 | 225 | 2.16 | 0.50 | 75685 | 0 | 75685 | 3200 | 1.87 | 63 | 34 | 97 | 0.5 |
| 24 | 254 | 0.62 | 0.13 | 40517 | 0 | 40517 | 288 | 0.81 | 54 | 0 | 54 | 2.7 |
| 44 | 259 | 0.25 | - | 11025 | 0 | 11025 | 6 | 0.49 | 1 | 0 | 1 | 5.2 |
| 55 | 266 | 2.00 | - | 18800 | 0 | 18800 | NA | 0.35 | 25 | 0 | 25 | 0.7 |
| 3 | 268 | 0.25 | 0.30 | 8816 | 0 | 8816 | 168 | 0.40 | 92 | 0 | 92 | 5.3 |
| 26 | 304 | 1.30 | - | 132506 | 3522 | 136027 | 516 | - | 81 | 2 | 84 | 1.1 |
| 49 | 322 | 0.50 | - | 75000 | 0 | 75000 | 950 | - | 75 | 25 | 100 | 3.2 |
| 6 | 428 | 1.00 | 0.80 | 118020 | 19 | 118039 | 20 | 0.80 | 6 | 82 | 89 | 2.2 |
| 48 | 435 | 1.30 | - | 89700 | 0 | 89700 | 20 | NA | 44 | 0 | 44 | 1.7 |
| 52 | 441 | 0.50 | 0.20 | 23480 | 0 | 23480 | 400 | 0.10 | 86 | 3 | 89 | 4.7 |
| 42 | 466 | 0.40 | 0.30 | 41086 | 0 | 41086 | 87 | - | 97 | 3 | 100 | 6.2 |
| 51 | 502 | 0.30 | - | 13200 | 0 | 13200 | 20 | NA | 89 | 6 | 95 | 8.4 |
| 5 | 514 | 1.30 | - | 36036 | 0 | 36036 | 500 | 1.00 | 100 | 0 | 100 | 2.0 |
| 33 | 518 | 0.85 | - | 39185 | 0 | 39185 | 1300 | 0.67 | 46 | 0 | 46 | 3.0 |
| 22 | 540 | 0.90 | - | 77715 | 0 | 77715 | 100 | 1.60 | 85 | 4 | 89 | 3.0 |
| 50 | 639 | 0.70 | 1.20 | 32940 | 0 | 32940 | 500 | 0.96 | 95 | 0 | 95 | 4.5 |
| 15 | 667 | 0.30 | 0.50 | 14946 | 0 | 14946 | 500 | 0.37 | 73 | 0 | 73 | 10.8 |
| 28 | 678 | 1.30 | NA | 184874 | 1 | 184874 | 10 | 1.08 | 13 | 41 | 54 | 2.6 |
| 7 | 724 | 0.61 | - | 19935 | 0 | 19935 | 5 | 0.63 | 96 | 0 | 96 | 5.9 |
| 9 | 741 | 0.74 | 1.50 | 43262 | 0 | 43262 | 44 | 1.60 | 83 | 3 | 86 | 4.9 |
| 11 | 777 | 0.80 | - | 74800 | 0 | 74800 | 100 | 1.12 | 58 | 10 | 68 | 4.9 |
| 47 | 789 | 0.32 | 0.45 | 40390 | 0 | 40390 | 47 | 0.8 | 76 | 0 | 76 | 11.6 |
| 27 | 870 | 1.68 | 2.50 | 331841 | 0 | 331841 | 652 | 1.28 | 49 | 29 | 78 | 2.5 |
| 32 | 908 | 1.10 | 0.60 | 59569 | 0 | 59569 | 1177 | 1.80 | 45 | 29 | 74 | 4.5 |
| 46 | 960 | 0.46 | 2.00 | 54408 | 0 | 54408 | 49 | 0.96 | 62 | 20 | 82 | 8.6 |
| 14 | 966 | 0.86 | 2.00 | 153941 | 0 | 153941 | 800 | 1.28 | 44 | 41 | 85 | 5.2 |
| 31 | 980 | 1.36 | 0.50 | 161135 | 0 | 161135 | 800 | 0.86 | 64 | 0 | 64 | 3.7 |
| 16 | 999 | 0.80 | - | 57226 | 0 | 57226 | 2000 | 1.00 | 69 | 9 | 78 | 6.2 |
| 13 | 1037 | 0.47 | 0.03 | 24497 | 0 | 24497 | 393 | 0.69 | 70 | 3 | 74 | 11.2 |
| 20 | 1045 | 1.00 | 1.70 | 97730 | 0 | 97730 | 10 | 0.87 | 58 | 13 | 71 | 4.9 |
| 30 | 1062 | 1.15 | 1.50 | 125595 | 0 | 125595 | 0 | 1.50 | 48 | 2 | 50 | 4.4 |
| 45 | 1117 | 0.30 | 0.10 | 29650 | 0 | 29650 | 350 | 1.2 | 59 | 0 | 59 | 18.9 |
| 2 | 1119 | 1.40 | - | 8484 | 327 | 8811 | 1000 | 1.00 | 5 | 1 | 6 | 3.8 |
| 43 | 1162 | 0.74 | 0.05 | 113959 | 0 | 113959 | 2123 | 1.79 | 48 | 22 | 70 | 7.9 |
| 10 | 1183 | 0.80 | 0.70 | 69905 | 0 | 69905 | NA | 1.90 | 60 | 8 | 67 | 7.5 |
| 36 | 1210 | 1.65 | 0.50 | 82303 | 0 | 82303 | 0.76 | 1.0 | 46 | 0 | 46 | 4.1 |
| 37 | 1242 | 1.91 | - | 139304 | 0 | 139304 | 49 | 1.46 | 50 | 17 | 67 | 3.3 |
| 12 | 1271 | 0.30 | 1.85 | 30474 | 0 | 30474 | 50 | 1.30 | 61 | 0 | 61 | 13.4 |
| 17 | 1370 | 0.67 | - | 4878 | 0 | 4878 | 16300 | 1.12 | 63 | 0 | 63 | 10.2 |
| 35 | 1443 | 1.04 | NA | 37551 | 0 | 37551 | 0 | 1.71 | 25 | 27 | 51 | 7.0 |
| 34 | 1530 | 1.99 | - | 208188 | 0 | 208188 | 50 | 1.95 | 51 | 7 | 58 | 3.8 |
| 38 | 1589 | 1.09 | NA | 88233 | 0 | 88233 | 4900 | 1.40 | 55 | 4 | 59 | 7.4 |
| 21 | 2417 | 3.10 | 2.30 | 157588 | 34220 | 191807 | 380 | 1.26 | 29 | 1 | 29 | 3.5 |
| 29 | 2564 | 1.05 | NA | 35244 | 0 | 35244 | 0 | 2.28 | 41 | 0 | 41 | 13.9 |

| Questionnaire ⁽¹⁾ | Specific SO ₂ (g/t crude treated) (²) | Sulphur in crude (%) | Sulphur in intermediate products (%) | Sulphur input in feedstock (t) ⁽³⁾ | Sulphur input in external fuels (t) | Total Sulphur input (t) | Sulphur in RFG (ppm) | Sulphur in liquid fuel (%) | RFG/total fuel burnt (%) | Natural gas/Total fuel burnt (%) | Total gas/Total fuel burnt (%) | Sulphur emitted in air/input (%) |
|--|---|-------------------------|--|--|--|----------------------------|-------------------------|-------------------------------|-----------------------------|-------------------------------------|-----------------------------------|-------------------------------------|
| Number of values | 49 | 49 | 26 | 49 | 49 | 49 | 47 | 43 | 49 | 49 | 49 | 49 |
| Average | 798 | 0.95 | 0.86 | 71 900 | | 72 677 | 865 | 1.06 | 61 | 9.8 | 71 | 5.2 |
| 5th percentile | 52 | 0.25 | 0.035 | 8 729 | 0 | 8 813 | 0.228 | 0.125 | 9 | 0.0 | 27 | 0.5 |
| 50th percentile | 741 | 0.85 | 0.5 | 54 408 | 0 | 54 408 | 100 | 1 | 61 | 3.0 | 74 | 4.4 |
| 95th percentile | 1 565 | 2 | 2 | 175 378 | 204 | 189 034 | 2 877 | 2 | 100 | 38.2 | 100 | 12.7 |
| ⁽¹⁾ Refineries with no atmospheric distillation are excluded. ⁽²⁾ The feedstock is calculated as the sum of crude oil and eventual intermediates, with no specific ponderation. ⁽³⁾ When not available (3 sites), the sulphur content of intermediates has been assumed equal to the site crude oil. NA These data have not been made available to the TWG. (-) Not applicable. Source: [TWG data collection questionnaires] | | | | | | | | | | | | |

Main contributing processes and units

The main emission sources of SO₂ are the process furnaces/boilers, sulphur recovery units, FCC regenerators, flares, waste water stripping and incondensable off-gas incinerators, decoking operations and coke calcination. The CONCAWE 2006 investigation already referred to in this section gives an average distribution of the SO_x emissions from the 67 refineries studied, as shown in Table 3.7.

Table 3.7: SO₂ breakdown by main contributing units as an average from a sample of 67 European refineries

| SO ₂ emitted by: | Percentage of the sulphur refinery intake | Approximate percentage of refinery SO ₂ emissions |
|--------------------------------|---|--|
| Fuel fired in furnaces/boilers | 1.8 % | 48 % |
| FCC units | 0.4 % | 11 % |
| Sulphur recovery units | 0.6 % | 16 % |
| Flares | 0.7 % | 20 % |
| Miscellaneous | 0.2 % | 5 % |
| Total: | 3.7 % | 100 % |

For further details, site-level individual data collected through TWG questionnaires have been summarised in Table 3.8 for 57 European refineries. The first part of the table corresponds to the group of sites which do not operate a FCC unit, while FCC sites are gathered in the second part of this table (next page). These data show the distribution of SO₂ emissions according to the main contributing units or processes.

Table 3.8: SO₂ emissions and main contributing units for a sample of 57 European refineries

| Site label | Nelson Index | FCC? (yes=1) | Year | Total SO ₂ | | S emitted/S input (%) | | Furnaces + boilers | | CHPs + stand-alone gas turbines | | FCC | | SRU | | Flares | | Other | |
|------------|--------------|--------------|------|-----------------------|--------|-----------------------|------|--------------------|--------|---------------------------------|------|-------|-------|-------|------|--------|------|-------|---|
| | | | | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % |
| 41 | 6.5 | 0 | 2008 | 49 | 0.3 % | 5 | 10 % | NA | - | - | - | 36 | 73 % | 8 | 16 % | 0 | 0 % | | |
| 25 | 9.7 | 0 | 2007 | 812 | 0.5 % | 568 | 70 % | - | - | - | - | 244 | 30 % | 0 | 0 % | 0 | 0 % | | |
| 40 | 6.2 | 0 | 2008 | 162 | 0.6 % | 158 | 98 % | 0 | 0 % | - | - | 4 | 2 % | 0.02 | 0 % | 0 | 0 % | | |
| 55 | 5.1 | 0 | 2008 | 250 | 0.7 % | 111 | 44 % | NA | - | - | - | 142 | 57 % | NA | - | 0 | 0 % | | |
| 4 | 3.1 | 0 | 2008 | 386 | 0.8 % | 76 | 20 % | 0 | 0 % | - | - | 0 | 0 % | 310.2 | 80 % | 0 | 0 % | | |
| 26 | 10.8 | 0 | 2008 | 3 101 | 1.1 % | 2 639 | 85 % | 289 | 9.3 % | - | - | 5 | 0.2 % | 169 | 5 % | 0 | 0 % | | |
| 48 | 8.4 | 0 | 2007 | 3 000 | 1.7 % | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 56 | 12.4 | 0 | 2008 | 5 022 | 3.0 % | 3 603 | 72 % | 1 351 | 27 % | - | - | NA | - | NA | - | 68 | 1 % | | |
| 33 | 4.6 | 0 | 2008 | 2 386 | 3.0 % | 1 746 | 73 % | 188 | 8 % | - | - | 452 | 19 % | NA | - | 0 | 0 % | | |
| 2 | 11.2 | 0 | 2007 | 678 | 3.8 % | NA | - | - | - | - | - | NA | - | NA | - | NA | - | | |
| 52 | 10.9 | 0 | 2008 | 2 199 | 4.7 % | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 44 | 1.6 | 0 | 2007 | 1 144 | 5.2 % | 429 | 37 % | 0 | 0 % | - | - | NA | - | 4.6 | 0 % | 711 | 62 % | | |
| 3 | 5.7 | 0 | 2006 | 932 | 5.3 % | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 35 | 5.7 | 0 | 2008 | 5 228 | 7.0 % | 3 980 | 76 % | 2 | 0.04 % | - | - | 278 | 5 % | 870 | 17 % | 98 | 2 % | | |
| 38 | 7.3 | 0 | 2008 | 13 002 | 7.4 % | 9 737 | 75 % | 80 | 0.62 % | - | - | 2 006 | 15 % | 1 179 | 9 % | 0 | 0 % | | |
| 17 | 4.0 | 0 | 2008 | 997 | 10.2 % | 866 | 87 % | 49 | 4.9 % | - | - | 0 | 0 % | 82 | 8 % | 0 | 0 % | | |
| 29 | 9.4 | 0 | 2007 | 9 789 | 13.9 % | 9 637 | 98 % | NA | - | - | - | 0 | 0 % | 0 | 0 % | 0 | 0 % | | |
| 19 | 5.1 | 0 | 2008 | 981 | NA | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 23 | 8.4 | 0 | 2007 | 4 818 | NA | NA | - | NA | - | - | - | NA | - | NA | - | NA | - | | |
| 53 | 3.8 | 0 | 2008 | 675 | NA | 50 | 7 % | 0 | 0 % | - | - | 575 | 85 % | 50 | 7 % | 0 | 0 % | | |
| 39 | 8.2 | 1 | 2008 | 346 | 0.2 % | 38 | 11 % | 0 | 0 % | 68 | 20 % | 102 | 29 % | 138 | 40 % | 0 | 0 % | | |
| 18 | 12.9 | 1 | 2007 | 1 331 | 0.8 % | 304 | 23 % | 0 | 0 % | 42 | 3 % | 941 | 71 % | 0 | 0 % | 39 | 3 % | | |
| 5 | 6.8 | 1 | 2008 | 1 424 | 2.0 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 6 | 13.5 | 1 | 2008 | 5 302 | 2.2 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 27 | 10.8 | 1 | 2006 | 16 653 | 2.5 % | 8 337 | 50 % | 32 | 0.19 % | 2 630 | 16 % | 312 | 2 % | 4 955 | 30 % | 388 | 2 % | | |
| 28 | 9.4 | 1 | 2008 | 9 668 | 2.6 % | 152 | 2 % | 8 424 | 87 % | 251 | 3 % | 841 | 9 % | 0 | 0 % | 0 | 0 % | | |
| 24 | 4.9 | 1 | 2007 | 2 195 | 2.7 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 22 | 7.2 | 1 | 2007 | 4 665 | 3.0 % | 1 621 | 35 % | 131 | 2.8 % | 1 110 | 24 % | 1 802 | 39 % | NA | - | 0 | 0 % | | |
| 49 | 5.7 | 1 | 2008 | 4 823 | 3.2 % | NA | - | NA | - | 3 200 | 66 % | 200 | 4 % | NA | - | NA | - | | |
| 37 | 9.5 | 1 | 2008 | 9 055 | 3.3 % | 4 706 | 52 % | 0 | 0 % | 303 | 3 % | 3 430 | 38 % | 616 | 7 % | 0 | 0 % | | |
| 21 | 13.1 | 1 | 2007 | 13 602 | 3.5 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 31 | 6.7 | 1 | 2008 | 11 847 | 3.7 % | 5 098 | 43 % | 143 | 1.2 % | 896 | 8 % | 5 710 | 48 % | NA | - | 0 | 0 % | | |
| 34 | 8.6 | 1 | 2007 | 16 008 | 3.8 % | 11 587 | 72 % | 0 | 0 % | 2 137 | 13 % | 2 283 | 14 % | 0.2 | 0 % | 0 | 0 % | | |
| 36 | 10.1 | 1 | 2008 | 6 801 | 4.1 % | 3 470 | 51 % | 241 | 3.5 % | 941 | 14 % | 2 018 | 30 % | NA | - | 131 | 2 % | | |
| 30 | 6.3 | 1 | 2007 | 11 138 | 4.4 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 50 | 10.5 | 1 | 2008 | 2 951 | 4.5 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 32 | 11.4 | 1 | 2008 | 5 347 | 4.5 % | 4 193 | 78 % | 3 | 0.06 % | 708 | 13 % | 340 | 6 % | 103 | 2 % | 0 | 0 % | | |
| 57 | 8.2 | 1 | 2008 | 8 402 | 4.6 % | 2 781 | 33 % | 0 | 0 % | 2 243 | 27 % | 2 142 | 25 % | 244 | 3 % | 993 | 12 % | | |
| 11 | 6.2 | 1 | 2008 | 7 263 | 4.9 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 9 | 6.6 | 1 | 2008 | 4 245 | 4.9 % | 1 560 | 37 % | 0 | 0 % | 986 | 23 % | 1 688 | 40 % | 11 | 0 % | 0 | 0 % | | |
| 20 | 12.9 | 1 | 2007 | 9 658 | 4.9 % | 3 537 | 37 % | 0 | 0 % | 4 911 | 51 % | 976 | 10 % | 231 | 2 % | 0 | 0 % | | |
| 14 | 9.3 | 1 | 2008 | 15 991 | 5.2 % | 9 475 | 59 % | 0 | 0 % | 2 121 | 13 % | 2 604 | 16 % | 1 791 | 11 % | 0 | 0 % | | |
| 7 | 6.4 | 1 | 2008 | 2 365 | 5.9 % | 733 | 31 % | 0 | 0 % | 658 | 28 % | 943 | 40 % | 31 | 1 % | 0 | 0 % | | |
| 42 | 12.0 | 1 | 2008 | 5 089 | 6.2 % | 113 | 2 % | 2 | 0.04 % | 970 | 19 % | 1 535 | 30 % | 449 | 9 % | 2 020 | 40 % | | |
| 16 | 8.7 | 1 | 2008 | 7 148 | 6.2 % | 2 525 | 35 % | 0 | 0 % | 864 | 12 % | 1 771 | 25 % | 336 | 5 % | 1 652 | 23 % | | |
| 10 | 6.8 | 1 | 2007 | 10 469 | 7.5 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 43 | 8.7 | 1 | 2008 | 17 979 | 7.9 % | 9 218 | 51 % | 194 | 1.1 % | 3 779 | 21 % | 4 632 | 26 % | 156 | 1 % | 0 | 0 % | | |
| 51 | 8.4 | 1 | 2007 | 2 210 | 8.4 % | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 46 | 6.2 | 1 | 2008 | 9 326 | 8.6 % | 1 784 | 19 % | 0 | 0 % | 1 929 | 21 % | 1 331 | 14 % | 1 475 | 16 % | 2 807 | 30 % | | |

| Site label | Nelson Index | FCC? (yes=1) | Year | Total SO ₂ | | S emitted/S input (%) | | Furnaces + boilers | | CHPs + stand-alone gas turbines | | FCC | | SRU | | Flares | | Other | |
|-------------------------|--------------|--------------|------|-----------------------|---------------|-----------------------|------|--------------------|--------|---------------------------------|------|-------|------|-------|------|--------|------|-------|---|
| | | | | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % | t/yr | % |
| 15 | 6.9 | 1 | 2007 | 3 239 | 10.8 % | 1 328 | 41 % | 0 | 0 % | 543 | 17 % | 582.9 | 18 % | 32.4 | 1 % | 753 | 23 % | | |
| 13 | 6.0 | 1 | 2008 | 5 499 | 11.2 % | 1 591 | 29 % | 0 | 0 % | 602 | 11 % | 1 527 | 28 % | 167 | 3 % | 1 611 | 29 % | | |
| 47 | 11.6 | 1 | 2008 | 9 365 | 11.6 % | 3 061 | 33 % | 0 | 0 % | 1 712 | 18 % | 1 096 | 12 % | 20 | 0 % | 3 477 | 37 % | | |
| 12 | 9.0 | 1 | 2008 | 8 151 | 13.4 % | 5 903 | 72 % | 0 | 0 % | 1 652 | 20 % | 421 | 5 % | 166 | 2 % | 9 | 0 % | | |
| 45 | 8.4 | 1 | 2008 | 11 230 | 18.9 % | 6 874 | 61 % | 0 | 0 % | 3 595 | 32 % | 760 | 7 % | 0 | 0 % | 0 | 0 % | | |
| 54 | 5.4 | 1 | 2007 | 729 | NA | NA | - | NA | - | NA | - | NA | - | NA | - | NA | - | | |
| 1 | 6.2 | 1 | 2009 | 539 | NA | 23 | - | 454 | - | 62 | - | NA | - | NA | - | NA | - | | |
| 58 | 10.2 | 1 | 2008 | 13 127 | NA | 11 264 | 88 % | 0.8 | 0.01 % | 262 | | 724 | 6 % | 877 | 7 % | 0 | 0 % | | |
| No of values: | 57 | - | | 57 | 51 | 39 | 39 | 35 | 35 | 27 | 25 | 38 | 38 | 33 | 33 | 39 | 39 | | |
| Minimum: | - | - | | 49 | 0.2 % | 5 | 2 % | 0 | 0 % | 42 | 3 % | 0 | 0 % | 0 | 0 % | 0 | 0 % | | |
| 5th Percentile: | - | - | | 327 | 0.6 % | 49 | 7 % | 0 | 0 % | 64 | 3 % | 0 | 0 % | 0 | 0 % | 0 | 0 % | | |
| Average: | - | - | | 4 832 | 5.1 % | 4 050 | 49 % | 318 | 4 % | 1 451 | 20 % | 1 170 | 23 % | 438 | 9 % | 378 | 7 % | | |
| 95th Percentile: | - | - | | 15 994 | 12.5 % | 9 890 | 89 % | 608 | 15 % | 3 724 | 47 % | 3 610 | 71 % | 1 601 | 34 % | 2 099 | 37 % | | |
| Maximum: | - | - | | 17 979 | 18.9 % | 11 587 | 98 % | 8 424 | 87 % | 4 911 | 66 % | 5 710 | 85 % | 4 955 | 80 % | 3 477 | 62 % | | |

NA: These data have not been made available to the TWG.
(-) Not applicable.
Source: [TWG data collection questionnaires]

As shown in Figure 3.12 and Figure 3.13, no obvious correlation can be graphically observed, for the first group of sites (non-FCC operated) or for the second one (including FCC), between the sulphur emitted/input ratio calculated for these refineries and the respective weight of their different main contributing units or processes. In both cases, furnaces and boilers appear most often as the main contributors, which confirms the trend shown in Table 3.7. It is even truer if emissions from the entire energy system, including eventual CHPs and stand-alone gas turbines, are considered.

For the selected refineries operating a FCC, this unit generates a rather stable proportion, most often within 15 – 30 %, of the SO₂ site emissions. The important role played by sources involved in the ‘Other’ category should also be noted, when they exist. Even if their average weight reported to the overall European refining emissions is low (around 5 %, as shown in Table 3.7), they most often represent a major part of the individual site-level SO₂ emissions for the refineries concerned. These emissions come from:

- the incineration of waste water stripping and/or process incondensable off-gases, when they are eventually not recycled into the RFG treating system;
- the coke plants, when present, and especially the green coke calcination;
- the contribution of flares, which can be very significant, notably for refineries experiencing other than normal operating conditions, such as technical difficulties or major start-up/shutdown episodes.

Influence of crude sulphur content and the site refining overall configuration

An overview of the historic development of the distribution of sulphur output in European refineries is given in Table 3.9. It also presents the average sulphur recovery percentage in the western European refineries that has grown from about 10 % in the late 1970s to more than 45 % now. This table shows the reductions of sulphur content achieved in the oil products destined for combustion (so-called S in fuels) sold to customers. It can be noted that these reductions were achieved while direct sulphur emissions from the refineries have shown a decrease since 1995.

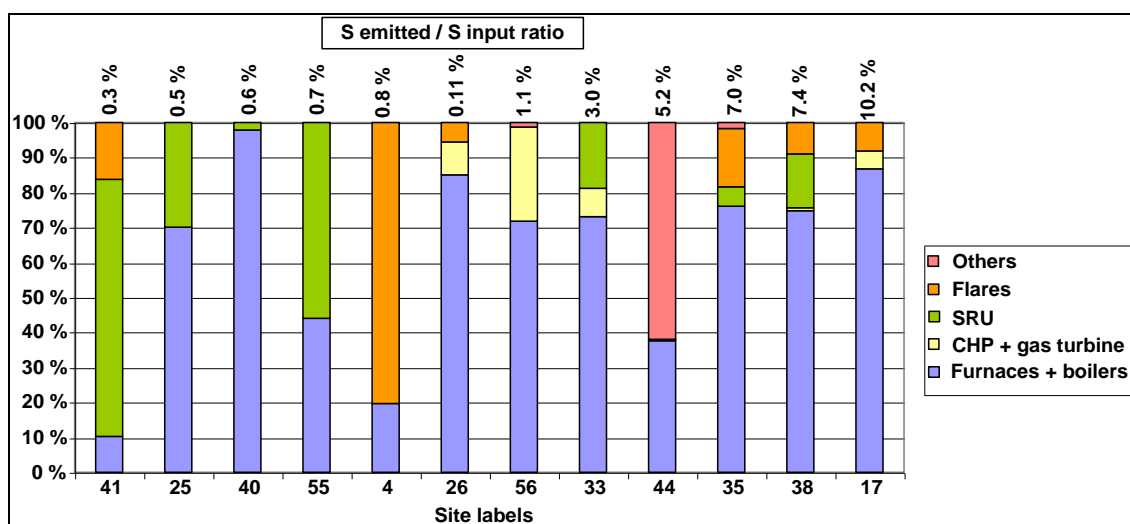


Figure 3.12: Respective weight of main SO₂-contributing processes for 12 European refineries not operating a FCC unit as a function of their sulphur emitted/input ratio

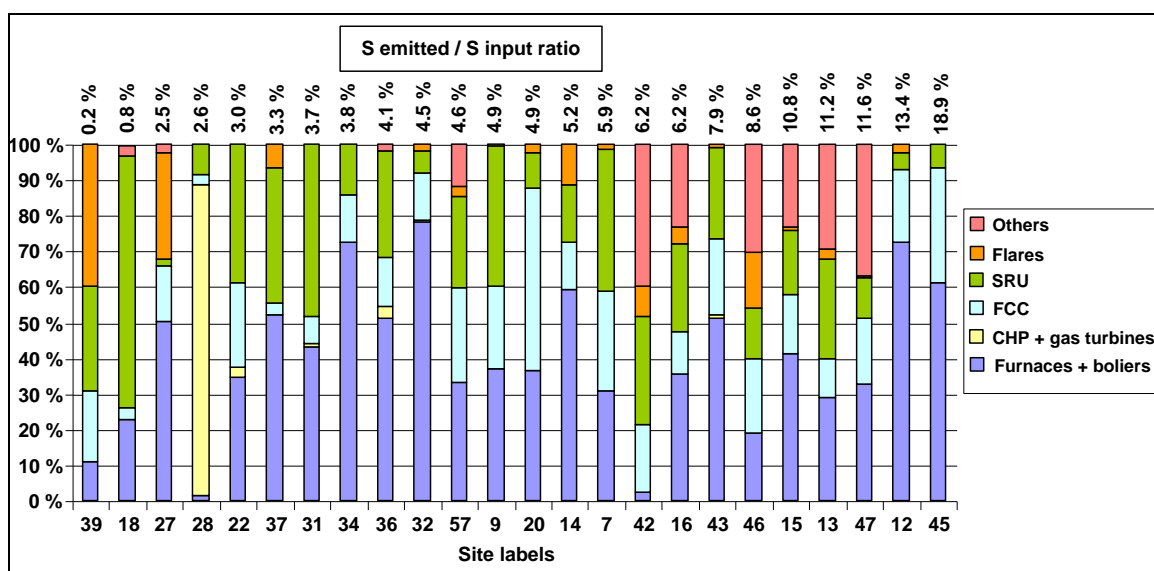


Figure 3.13: Respective weight of main SO₂-contributing processes for 24 European refineries operating a FCC as a function of their sulphur emitted/input ratio

Table 3.9: Trends of sulphur distribution in western European refineries (data in kt/yr)

| Year | 1979 | 1982 | 1985 | 1989 | 1992 | 1995 | 1998 | 2002 | 2006 |
|------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Crude intake ⁽¹⁾ | 680000 | 494000 | 479000 | 527000 | 624000 | 637000 | 635000 | 684000 | 696000 |
| S in crude % ⁽²⁾ | 1.45 | 1.28 | 0.98 | 1.10 | 1.06 | 1.03 | 0.97 | 0.91 | 0.91 |
| S in crude ⁽¹⁾ | 9860 | 6323 | 4694 | 5797 | 6615 | 6561 | 6159 | 6224 | 6334 |
| S recovered % ⁽²⁾ | 10.4 | 17.5 | 23.2 | 30.5 | 26.9 | 36.1 | 39.4 | 47.6 | 45.0 |
| S emitted in air % | 9.0 | 12.2 | 11.2 | 9.1 | 7.9 | 8.6 | 7.2 | 5.5 | 3.7 |
| S in fuels % ⁽²⁾ | 90.7 | 75.7 | 73.3 | 58.3 | 50.9 | 40.0 | 37 | 29.8 | 32.5 |

⁽¹⁾ For all OECD Europe.

⁽²⁾ From the CONCAWE refinery site sample covered by the annual survey.

Source: [152, CONCAWE 1998] [63, CONCAWE 2010]

Figure 3.14 shows, for 51 European refineries, the interaction between various parameters related to the crude quality (% of sulphur), the site complexity (measured with the Nelson Index), and the specific emissions reported to the amount of feedstock treated (SO₂ g/t) and to

the sulphur total intake (% of sulphur emitted/input ratio). Available data are displayed for two site groups according to the presence of a FCC unit (34 sites) or not (17 sites).

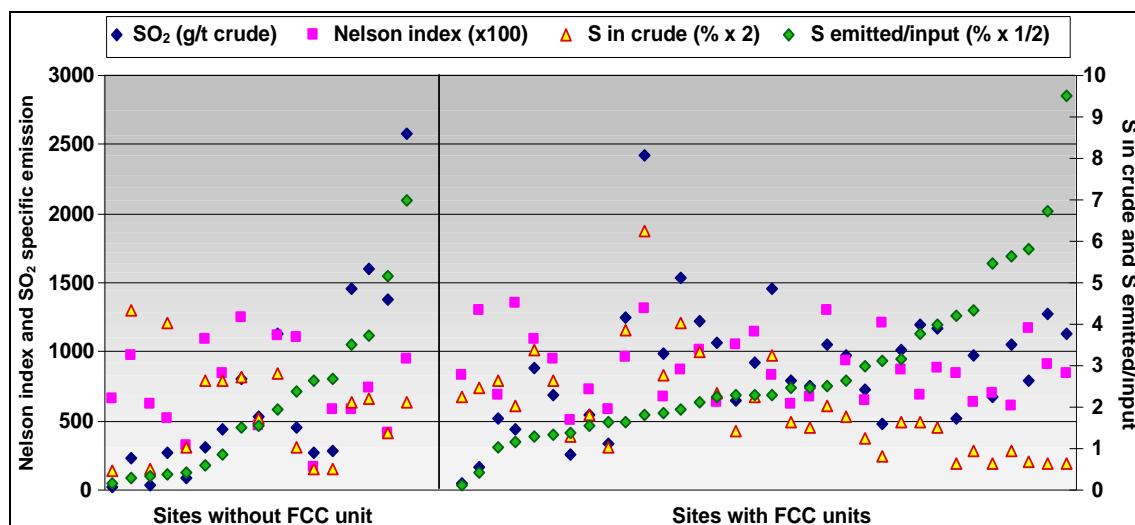


Figure 3.14: Influence of the configuration, complexity and crude quality on SO₂ emissions

Several points can be derived from this graphic.

- The highest SO₂ specific emissions are not necessarily associated with the most complex sites.
- As mentioned at the beginning of this section, FCC units contribute to around 11 % of the SO₂ European refining emissions, and represent on average 20 % (up to 66 %) of the individual emissions of the sites concerned. However, as shown in Figure 3.14, refineries with FCC do not tend to emit more SO₂ than refineries without FCC.
- Another important variable that is typically referred to for explaining the behaviour of SO₂ emissions in refineries is the content of sulphur in the crude oil processed. However, once again, data displayed in Figure 3.14 show that, within this site sample, refineries with similar sulphur content in the treated crude oil can have very high differences in specific emissions, and many sites achieving very high specific emissions are actually those treating the most favourable crudes.

Influence of the refinery fuel mix

Another parameter which could be expected to strongly influence the refinery SO₂ emissions is the ratio of gaseous fuels (including the eventual supply of external natural gas) and residual liquid fuels in the site energy supply. As shown in Figure 3.15, there is a clear correlation within this site sample between the SO₂ specific emissions and the weight of residual fuel oils in the fuel mix, even if some sites with very high liquid fuel ratios can achieve a very good SO₂ performance.

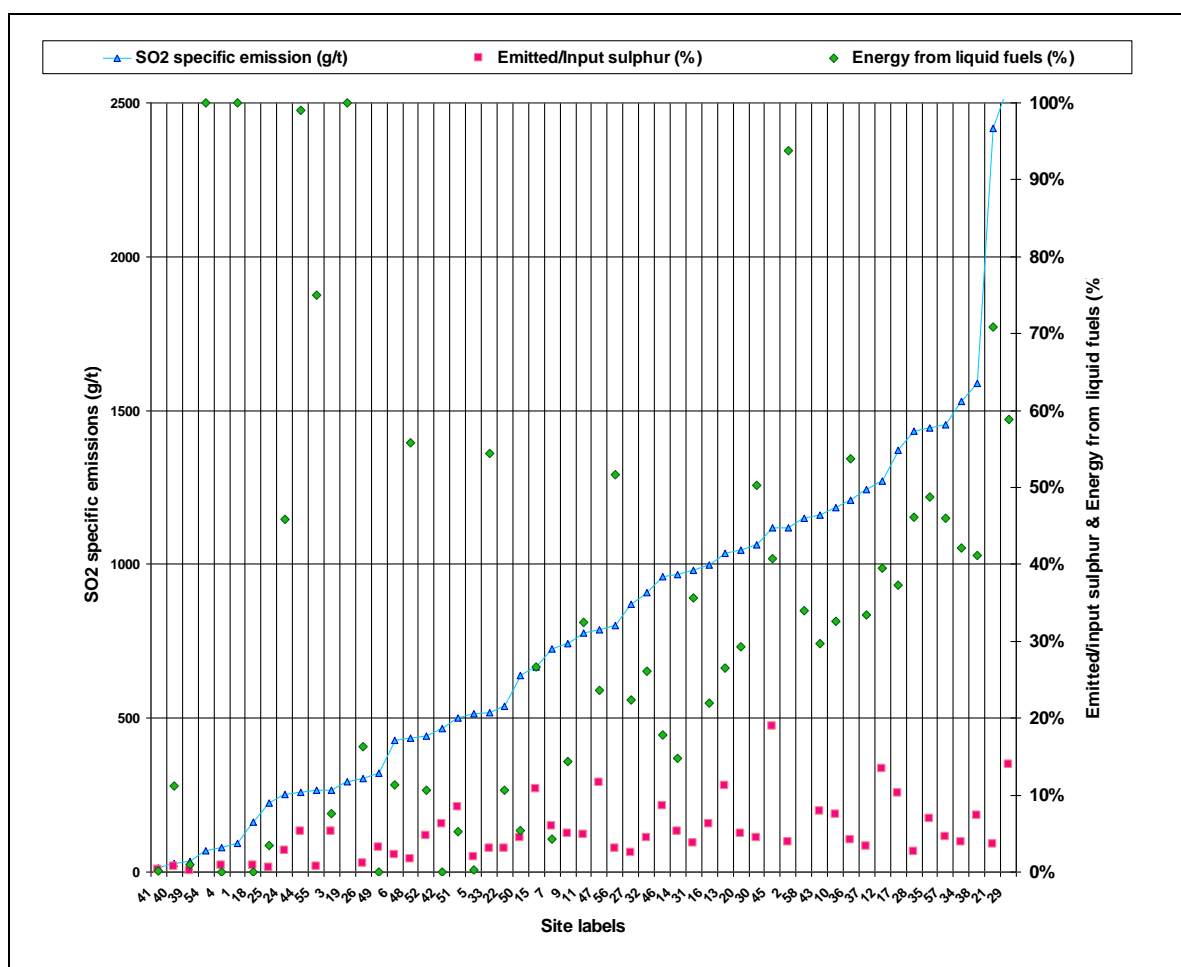


Figure 3.15: Influence of the gaseous fuels used for energy supply on the site SO₂ emissions

3.1.2.5 Volatile organic compounds emissions

Volatile organic compounds (VOCs) is the generic term applied to all compounds containing organic carbon, which evaporate at ambient temperature and contribute to the formation of odour nuisance, 'summer smog' and, with sufficient sunshine, tropospheric ozone. VOC losses can be calculated through various methods based on emission factors or directly measured. Extensive information on this issue can be found in Section 3.26.1.3 related specifically to VOC monitoring.

The main sources of VOCs from refineries are fugitive emissions from piping systems, waste water systems, fixed roof storage tanks (tank breathing), loading and unloading systems, other storage, handling, and blowdown systems. Fugitive VOC emission sources such as (single) seals from pumps, compressors, valves and flanges and leaks in pipelines and equipment may contribute significantly to the total VOC emissions. Most of the European refineries (from 5th to 95th percentiles based on the 53 sites gathered by the TWG) emit from 150 to 6 500 tonnes of VOCs per year; the related specific emission range is from 50 to 1 000 tonnes of VOCs per million tonnes of total feed processed. Almost all of these results have been achieved using emission factor estimates. All available data are displayed in Table 3.10. For more details on diffuse VOC monitoring, see Section 3.26.1.3.

Table 3.10: Data on volatile organic compounds emitted by a sample of 53 European refineries

| Site label | Nelson Index | Total VOCs | | NMVOC | | Diffuse VOCs | | Benzene | |
|------------------------|--------------|-------------|-------------|-------------|------------|--------------|------------|--------------|------------|
| | | t/yr | g/t | t/yr | g/t | t/yr | g/t | kg/yr | g/t |
| 44 | 1.6 | 1621 | 368 | NA | NA | 1563 | 354 | 48642 | 11.03 |
| 4 | 3.1 | 6882 | 1404 | 4792 | 978 | NA | NA | NA | NA |
| 17 | 4.0 | 282 | 387 | NA | NA | NA | NA | 3585 | 4.92 |
| 33 | 4.6 | NA | NA | 1170 | 254 | NA | NA | NA | NA |
| 24 | 4.9 | NA | NA | NA | NA | 3825 | 442 | NA | NA |
| 19 | 5.1 | 2825 | 841 | NA | NA | NA | NA | NA | NA |
| 55 | 5.1 | NA | NA | 435 | 463 | 435 | 463 | NA | NA |
| 54 | 5.4 | NA | NA | 6161 | 571 | NA | NA | NA | NA |
| 35 | 5.7 | 2388 | 659 | 2012 | 555 | NA | NA | 416 | 0.11 |
| 49 | 5.7 | 956 | 64 | 913 | 61 | 758 | 51 | 6742 | 0.45 |
| 3 | 5.7 | 1231 | 353 | 1192 | 342 | NA | NA | NA | NA |
| 13 | 6.0 | NA | NA | 1176 | 222 | NA | NA | 31710 | 5.98 |
| 40 | 6.2 | NA | NA | 3000 | 529 | 3000 | 529 | 34000 | 6.00 |
| 1 | 6.2 | NA | NA | 503 | 55 | NA | NA | NA | NA |
| 11 | 6.2 | NA | NA | 1390 | 149 | 233 | 25 | 11697 | 1.25 |
| 46 | 6.2 | NA | NA | NA | NA | 1021 | 105 | NA | NA |
| 30 | 6.3 | NA | NA | 2103 | 200 | 2040 | 194 | 41130 | 3.92 |
| 7 | 6.4 | 513 | 157 | NA | NA | NA | NA | 12983 | 3.97 |
| 41 | 6.5 | 1071 | 272 | NA | NA | 905 | 230 | 14000 | 3.55 |
| 9 | 6.6 | 1077 | 188 | 795 | 139 | 94 | 16 | 14649 | 2.56 |
| 31 | 6.7 | NA | NA | 806 | 67 | NA | NA | 6490 | 0.54 |
| 5 | 6.8 | NA | NA | NA | NA | 923 | NA | NA | NA |
| 10 | 6.8 | 997 | 113 | 967 | 109 | 897 | 101 | 16177 | 1.83 |
| 15 | 6.9 | 558 | 115 | NA | NA | NA | NA | 6000 | 1.24 |
| 22 | 7.2 | NA | NA | 3095 | 358 | 3022 | 350 | 33346 | 3.86 |
| 39 | 8.2 | NA | NA | 3910 | 387 | 3910 | 387 | 38000 | 3.76 |
| 57 | 8.2 | 1175 | 203 | 1123 | 194 | 1019 | 176 | NA | NA |
| 45 | 8.4 | 4300 | 428 | 4270 | 425 | 4100 | 408 | 40000 | 3.98 |
| 23 | 8.4 | NA | NA | 2900 | NA | NA | NA | 24008 | NA |
| 48 | 8.4 | 32000 | 4638 | 1000 | 145 | NA | NA | 17835 | 2.58 |
| 51 | 8.4 | 666 | 151 | 646 | 147 | NA | NA | 2034 | 0.46 |
| 34 | 8.6 | 1750 | 167 | 1537 | 147 | NA | NA | NA | NA |
| 16 | 8.7 | NA | NA | 768 | 107 | NA | NA | NA | NA |
| 43 | 8.7 | 2056 | 133 | 2006 | 130 | NA | NA | 35000 | 2.26 |
| 12 | 9.0 | NA | NA | 677 | 106 | NA | NA | 13889 | 2.17 |
| 14 | 9.3 | NA | NA | 2252 | 136 | 2355 | 142 | 25251 | 1.53 |
| 29 | 9.4 | NA | NA | 780 | 204 | 738 | 193 | 17000 | 4.45 |
| 28 | 9.4 | 1110 | 78 | NA | NA | 774 | 54 | 1003 | 0.07 |
| 37 | 9.5 | 5651 | 775 | 4862 | 667 | 4490 | 616 | 1660 | 0.23 |
| 25 | 9.7 | 236 | 65 | NA | NA | 236 | 65 | NA | NA |
| 36 | 10.1 | 152 | 27 | 151 | 27 | NA | NA | NA | NA |
| 58 | 10.2 | 2227 | 195 | NA | NA | 2086 | 183 | NA | NA |
| 50 | 10.5 | 2552 | 552 | 2376 | 514 | 2271 | 492 | 4216 | 0.91 |
| 27 | 10.8 | 3070 | 160 | 2757 | 144 | 207 | 11 | 10000 | 0.52 |
| 26 | 10.8 | 2103 | 206 | 2082 | 204 | 1958 | 192 | 43752 | 4.29 |
| 52 | 10.9 | 807 | 162 | 783 | 157 | NA | NA | 9600 | 1.92 |
| 2 | 11.2 | 151 | 249 | NA | NA | NA | NA | NA | NA |
| 32 | 11.4 | 742 | 126 | 709 | 120 | 67 | 11 | 5300 | 0.90 |
| 47 | 11.6 | 4949 | 417 | NA | NA | NA | NA | 64320 | 5.42 |
| 42 | 12.0 | 6044 | 554 | 5971 | 547 | 5850 | 536 | 302000 | 27.67 |
| 56 | 12.4 | NA | NA | 123 | 20 | NA | NA | NA | NA |
| 20 | 12.9 | NA | NA | 3655 | 395 | NA | NA | 32894 | 3.56 |
| 21 | 13.1 | 3326 | 591 | NA | NA | 3288 | 584 | NA | NA |
| No of values | | 32 | 32 | 38 | 37 | 28 | 27 | 34 | 33 |
| 5th percentile | | 198 | 65 | 392 | 50 | 134 | 13 | 1430 | 0.2 |
| 50th percentile | | 1426 | 205 | 1291 | 194 | 1292 | 193 | 15413 | 2.6 |
| 95th percentile | | 6421 | 1095 | 5029 | 590 | 4353 | 570 | 54129 | 8.0 |

Figure 3.16 has been constructed from the 39 refineries in this sample for which the full distribution of VOCs (Total VOC or NMVOC) per contributing processes has been made available.

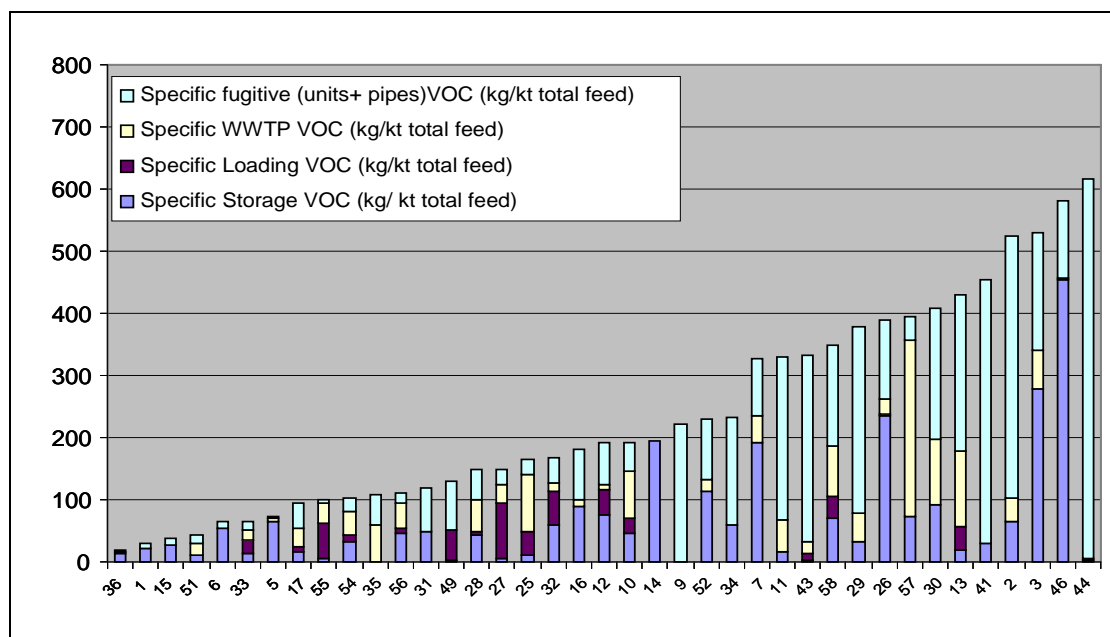


Figure 3.16: VOC specific emission range and breakdown for 39 European refineries

As it appears in Figure 3.16, the highest specific VOC emissions at the site level are mainly driven by fugitive emissions (leakages from units and pipes) and storage emissions. For the lowest ones, the waste water treatment is the most significant.

Some accidental spillages can be of a continuous nature, such as leaking pump seals, leaking valve glands and leaks from pipework. Others, which are of a one-off nature, can occur from sources such as equipment failures, overfilling of tanks and overfilling of road and rail cars. As shown in Figure 3.16 from the TWG 2008 data collection, the fugitive emissions from process equipment are one of the largest single sources of VOCs emitted to the atmosphere in a refinery and can account for 50 % of the total emissions. Fugitive emissions include the emissions that occur from items such as valves, pump and compressor seals, flanges, vents and open ends. Valves are considered to account for approximately 50–60 % of fugitive emissions. Furthermore, a major portion of fugitive emissions comes from only a small fraction of the sources (e.g. less than 1 % of valves in gas/vapour service can account for over 70 % of the fugitive emissions of a refinery). Some valves are more likely to leak than others, e.g.:

- Valves that are operated frequently, such as control valves, may wear down more quickly and allow emission paths to develop. However, newer, low-leak control valves provide a good fugitive emissions control performance.
- Valves with rising stems (gate valves, globe valves) are likely to leak more frequently than quarter-turn type valves such as ball and plug valves.

Factors driving these releases of hydrocarbons are equipment design, quality of the sealing system, maintenance programme and properties of the line contents. Poor designs (with wider tolerances), poor sealing systems (e.g. leak-prone valve packings) and limited maintenance will lead to higher emissions. These emissions can be estimated using the factors in Table 3.11.

For example emission factors can be estimated, using the US EPA stratified method as presented in Table 3.15, taking into account that they are derived from short-term

measurements. Other methods have been applied to calculate the fugitive emissions from refineries, the adsorption method and DIAL method (see Section 3.26).

Table 3.11: Emission factors according to the stratified US EPA method for the assessment of fugitive emissions

| Emission source | Emission factor in (g/(h. source)) for measured values in ppm v/v in the following three ranges | | |
|--|---|--------------|-------------|
| | 0 – 1000 | 1001 – 10000 | >10000 |
| Emission range (ppm v/v) | | | |
| Valves for gas or vapour | 0.14 | 1.65 | 45.1 |
| Valves for liquids with Vp>0.3 kPa (light liquids) | 0.28 | 9.63 | 85.2 |
| Valves for liquids with Vp<0.3 kPa (heavy liquids) | 0.23 | 0.23 | 0.23 |
| Pumps for light liquids | 1.98 | 33.5 | 437 |
| Pumps for heavy liquids | 3.80 | 92.6 | 389 |
| Compressors | 11.32 | 264 | 1 608 |
| Safety valves for gases | 11.4 | 279 | 1 691 |
| Flanges | 0.02 | 8.75 | 37.5 |
| Open-end valves | 0.13 | 8.76 | 12.0 |
| <i>Source: [160, Janson 1999] [77, REF TWG 2010]</i> | | | |

3.1.2.6 Other emissions to air

Other pollutants considered are carbon monoxide (process furnaces/boilers, gas turbines, FCC regenerators, flare system, incinerators, cold vents) and methane (storage and handling (loading), cold vents and leaks). Noise, H₂S, NH₃, CS₂, dioxins and HF also contribute to the air emissions from a refinery.

Mercury and components of arsenic are volatile and are emitted to some extent with the clean gas. A part of these compounds react with plant material or deposit on the catalysts in the reactors of the conversion plants. Therefore, protective layers are used for the interception of the catalyst poisons.

Flares, compressors, pumps, turbines and air coolers require particular attention as regards sources of noise.

Finally, odours in a refinery are mainly created by sulphur compounds such as H₂S, mercaptans but also by some hydrocarbons (e.g. aromatics). The main sources of odour in refineries are storage (e.g. sour crudes), bitumen production, water desalter, sewers, uncovered dissolved air flotation, oil/water/solid separation and biotreatment units and flaring.

Table 3.12 gathers a set of data illustrating the performance of European refineries, made available from the 61 site-level questionnaires provided by the TWG in charge of the revision of the present document.

Table 3.12: Specific air emission ranges for various substances from European refineries

| Substance | Specific load (g/t of feed) | | No of values |
|----------------------------------|-----------------------------|-----------------|----------------|
| | 5th – 95th percentile | 50th percentile | |
| Carbon monoxide | 10 – 415 | 53 | 43 |
| Ammonia | 0.1 – 22 | 1.1 | 17 |
| Hydrogen sulphide | 0.15 – 1.1 | 0.3 | 4 |
| Hydrofluoric acid ⁽¹⁾ | 0.01 – 1.6 | 0.1 | 6 |
| Benzene | 0.18 – 8 | 2.5 | 33 |
| BTEX | 1 – 70 | 17 | 7 |
| PAH-16 | 0.001 – 0.4 | 0.005 | 17 |
| PCDD/F | NA | NA | |
| As | <0.001 – 0.014 | 0.002 | 28 |
| Cd | <0.001 – 0.034 | 0.002 | 25 |
| Cr | <0.001 – 0.18 | 0.007 | 29 |
| Cu | <0.001 – 0.07 | 0.009 | 24 |
| Hg | <0.0001 – 0.038 | 0.001 | 23 |
| Mn ⁽¹⁾ | 0.002 – 0.007 | 0.004 | 3 |
| Ni | 0.002 – 1.3 | 0.16 | 37 |
| Pb | 0.001 – 0.1 | 0.009 | 27 |
| Se ⁽¹⁾ | 0.002 – 0.007 | 0.004 | 3 |
| V | 0.001 – 1.1 | 0.15 | 23 |
| Zn | 0.001 – 0.62 | 0.04 | 33 |
| Metals ⁽²⁾ | 0.01 – 3.4 | 0.38 | ⁽²⁾ |

⁽¹⁾ For these parameters, only min., max. and average are provided given the limited number of available values.

⁽²⁾ Sum of individual percentile data for the following metals:
Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, Zn.

3.1.2.7 Expression of full or partial site air emissions using ‘bubbles’

The ‘bubble’ approach for the evaluation and monitoring of refinery air emissions

In the context of this BREF and for the purpose of expressing meaningful site or partial site emissions level, the bubble determination should always be based on concentration and specific emission ranges expected at all concerned installations when BAT is applied, and should involve the following steps (regardless of their order):

1. exhaustive identification and geographical mapping of all included sources;
2. determination of the off-gas volumetric contributions expected from all included sources;
3. determination of the mass contributions expected from all included sources;
4. determination of the bubble-associated monitoring regime.

The actual details of the calculation and additional information on each of these steps are given in Annex 8.6. More details on this approach are available in Section 4.15.5.

The total emissions of one substance released by all the stacks on site can therefore be expressed as a single value using this approach based on available data provided through the TWG data collection.

Actual NO_x emissions from European refineries: bubble-expressed examples

Site individual sets of NO_x data collected by the TWG for each site have been gathered in Table 3.13. These data have been processed in order to calculate the annual average equivalent concentration of NO_x in the sum of flue-gases emitted by the four categories of contributing units as listed below. These calculations are based on actual emissions reported for the year 2007 or 2008. Two examples of bubble-expressed emission levels, which correspond respectively to Figure 3.17 and Figure 3.18, are presented for the set of sites concerned.

In the first case, as shown in Figure 3.17, which corresponds to Column (e) in Table 3.13, the full list of contributors has been used, which includes:

- furnaces and boilers
- CHPs and gas turbines
- FCC units
- sulphur recovery units.

Mass and volumetric contribution terms from each of these four categories were fully available for a sample of 25 sites, of which seven were non-FCC sites and 18 were FCC sites; Figure 3.17 shows the range of equivalent concentrations obtained. The unit for which less data were available, in particular as far as volumetric contributions were concerned, is SRU and is mainly responsible for the limited size of this refinery set.

In the second case, illustrated by Figure 3.18, the small NO_x contribution of sulphur recovery units has not been taken into account, and contributors only include:

- furnaces and boilers
- CHPs and gas turbines
- FCC units.

Mass and volumetric contribution from each of these three categories were fully available for a total of 30 sites, of which 10 were non-FCC sites and 20 were FCC sites. The results obtained for the whole group of refineries are very close to the results obtained in the first case.

In both cases, as shown in Figure 3.17 and Figure 3.18, an information summary is provided for each refinery on the part taken by the refinery fuel gas and an eventual additional natural gas supply in the refinery energy mix, together with the main NO_x abatement techniques implemented on the FCC unit and the energy system.

Table 3.13: Equivalent concentrations of NO_x emissions for a sample of European refineries

| Questionnaire | Configuration with FCC? | Specific NO _x emission | Furnace +boilers | | CHP + gas turbines | | FCC | | SRU | | Bubble CP (a) | Bubble CP+CHP (b) | Bubble CP+CHP+SRU (c) | Bubble FCC (d) | Full bubble (e) |
|---|-------------------------|-----------------------------------|------------------|--|--------------------|----------------------|------|----------------------|------|----------------------|---------------|-------------------|-----------------------|----------------|-----------------|
| | | | t/yr | GNm ³ /yr | t/yr | GNm ³ /yr | t/yr | GNm ³ /yr | t/yr | GNm ³ /yr | | | | | |
| | | yes=1 | g/t | mg/Nm ³ at 3 % O ₂ | | | | | | | | | | | |
| 40 | 0 | 59 | 328 | 3.48 | 0 | 0.00 | - | - | 7.7 | 0.09 | 94 | 94 | 94 | - | 94 |
| 53 | 0 | 69 | 375 | 2.09 | 0 | 0.00 | - | - | 3 | 0.02 | 179 | 179 | 179 | - | 179 |
| 25 | 0 | 81 | 270 | 2.16 | 0 | 0.00 | - | - | 24.2 | 0.10 | 125 | 125 | 130 | - | 130 |
| 26 | 0 | 89 | 536 | 6.15 | 366 | 1.51 | - | - | 1.66 | 0.06 | 87 | 118 | 117 | - | 117 |
| 44 | 0 | 108 | 389 | 0.88 | 0 | 0.00 | - | - | NA | NA | 442 | 442 | NA | - | NA |
| 56 | 0 | 210 | 824 | 2.64 | 431 | 0.98 | - | - | NA | NA | 312 | 347 | NA | - | NA |
| 33 | 0 | 374 | 887 | 1.73 | 814 | 0.86 | - | - | 24 | 0.03 | 512 | 655 | 656 | - | 656 |
| 38 | 0 | 392 | 2316 | 4.73 | 870 | 1.32 | - | - | NA | 0.16 | 490 | 527 | 513 | - | 513 |
| 35 | 0 | 424 | 927 | 1.75 | 609 | 0.27 | - | - | 0.00 | 0.35 | 529 | 757 | 645 | - | 645 |
| 8 | 0 | 500 | 476 | 2.20 | 0 | 0.00 | - | - | NA | NA | 216 | 216 | NA | - | NA |
| 39 | 1 | 68 | 620 | 6.03 | 0 | 0.00 | 48 | 0.73 | 0 | 0.19 | 103 | 103 | 100 | 66 | 96 |
| 1(f) | 1 | 92 | 221 | 3.03 | 454 | 5.61 | 88 | 0.76 | NA | NA | 73 | 78 | 78 | 116 | 78 |
| 49 | 1 | 93 | 760 | 5.60 | 300 | 0.60 | 300 | 2.00 | 20 | 0.08 | 136 | 171 | 172 | 150 | 167 |
| 18 | 1 | 138 | 959 | 6.20 | 0 | 0.00 | 127 | 0.84 | 20.7 | 0.11 | 155 | 155 | 155 | 151 | 155 |
| 46 | 1 | 173 | 1322 | 4.00 | 101 | 0.66 | 187 | 1.70 | NA | NA | 331 | 305 | NA | 110 | NA |
| 47 | 1 | 217 | 2002 | 7.81 | 0 | 0.00 | 575 | 1.98 | 0 | 0.02 | 256 | 256 | 256 | 290 | 263 |
| 14 | 1 | 231 | 2554 | 10.12 | 661 | 5.55 | 540 | 0.94 | 34 | 0.37 | 252 | 205 | 203 | 574 | 223 |
| 22 | 1 | 237 | 1052 | 4.25 | 498 | 5.95 | 481 | 1.74 | 17.4 | 0.14 | 247 | 152 | 151 | 276 | 169 |
| 9 | 1 | 248 | 557 | 2.26 | 532 | 0.60 | 324 | 0.70 | 0 | 0.03 | 246 | 380 | 376 | 467 | 394 |
| 42 | 1 | 249 | 1056 | 4.74 | 154 | 0.56 | 178 | 1.13 | 21 | 0.06 | 223 | 255 | 256 | 158 | 238 |
| 32 | 1 | 254 | 783 | 3.13 | 410 | 1.15 | 265 | 0.71 | NA | NA | 250 | 279 | NA | 373 | NA |
| 27 | 1 | 259 | 3608 | 11.91 | 920 | 7.58 | 357 | 1.43 | 14 | 0.65 | 303 | 232 | 226 | 250 | 227 |
| 57 | 1 | 266 | 1261 | 5.61 | 0 | 0.00 | 229 | 0.90 | 13 | 0.17 | 225 | 225 | 220 | 254 | 225 |
| 7 | 1 | 301 | 742 | 1.54 | 43 | NA | 177 | 0.38 | 22 | 0.05 | 482 | NA | NA | 466 | NA |
| 20 | 1 | 318 | 1589 | 6.40 | 607 | 3.10 | 706 | 1.90 | 40 | 0.10 | 248 | 231 | 233 | 372 | 256 |
| 12 | 1 | 339 | 1608 | 5.03 | 0 | 0.00 | 561 | 1.31 | 0 | 0.05 | 320 | 320 | 317 | 428 | 339 |
| 43 | 1 | 375 | 3339 | 7.20 | 1068 | 1.00 | 1396 | 2.51 | 0 | 0.10 | 464 | 537 | 531 | 556 | 537 |
| 36 | 1 | 394 | 1304 | 8.24 | 644 | 2.62 | 252 | 1.40 | 0 | NA | 158 | 179 | NA | 180 | NA |
| 13 | 1 | 406 | 1419 | 3.39 | 0 | 0.00 | 618 | 1.24 | 0 | 0.08 | 418 | 418 | 408 | 497 | 431 |
| 28 | 1 | 431 | 968 | 5.45 | 4523 | 11.58 | 626 | 0.85 | 30 | 0.34 | 177 | 322 | 318 | 735 | 337 |
| 45 | 1 | 453 | 1340 | 3.68 | 2080 | 3.71 | 1125 | 3.95 | 10 | 0.05 | 364 | 463 | 461 | 285 | 400 |
| 37 | 1 | 575 | 1728 | 4.85 | 1792 | 1.79 | 381 | 1.25 | 1.2 | 0.08 | 356 | 530 | 524 | 305 | 489 |
| No of values | | 32 | 32 | 32 | 32 | 31 | 22 | 22 | 25 | 26 | 32 | 31 | 25 | 22 | 25 |
| Average | | 263 | 1191 | 5 | 559 | 1.84 | 434 | 1.38 | 12 | 0 | 274 | 299 | 293 | 321 | 294 |
| Minimal | | 59 | 221 | 0.88 | 0 | 0.00 | 48 | 0.38 | 0 | 0.00 | 73 | 78 | 78 | 66 | 78 |
| 5th percentile | | 69 | 302 | 1.65 | 0 | 0.00 | 127 | 0.70 | 0 | 0.02 | 91 | 99 | 95 | 110 | 94 |
| 50th percentile | | 252 | 964 | 4.49 | 366 | 0.63 | 357 | 1.25 | 10 | 0.09 | 249 | 255 | 233 | 288 | 238 |
| 95th percentile | | 474 | 2907 | 9.09 | 1922 | 6.77 | 1125 | 2.51 | 33 | 0.37 | 499 | 596 | 622 | 574 | 624 |
| Maximal | | 575 | 3608 | 11.91 | 4523 | 11.58 | 1396 | 3.95 | 40 | 0.65 | 529 | 757 | 656 | 735 | 656 |
| (a) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers. | | | | | | | | | | | | | | | |
| (b) Equivalent concentration calculated for off-gases emitted by all furnaces, boilers, and CHP and stand-alone gas turbines if any. | | | | | | | | | | | | | | | |
| (c) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers, CHP and stand-alone gas turbines if any, and SRUs. | | | | | | | | | | | | | | | |
| (d) Equivalent concentration corresponding to the FCC alone. | | | | | | | | | | | | | | | |
| (e) Equivalent concentration corresponding to the sum of (c) and off-gases emitted by the FCC units if any. | | | | | | | | | | | | | | | |
| (f) NB: Site 1 data made available for 2 009 emissions- tail gas of SRU treated in SNO _x of CHP plant. | | | | | | | | | | | | | | | |
| NB: NA These data have not been made available to the TWG. | | | | | | | | | | | | | | | |
| Source: [TWG data collection questionnaires] | | | | | | | | | | | | | | | |

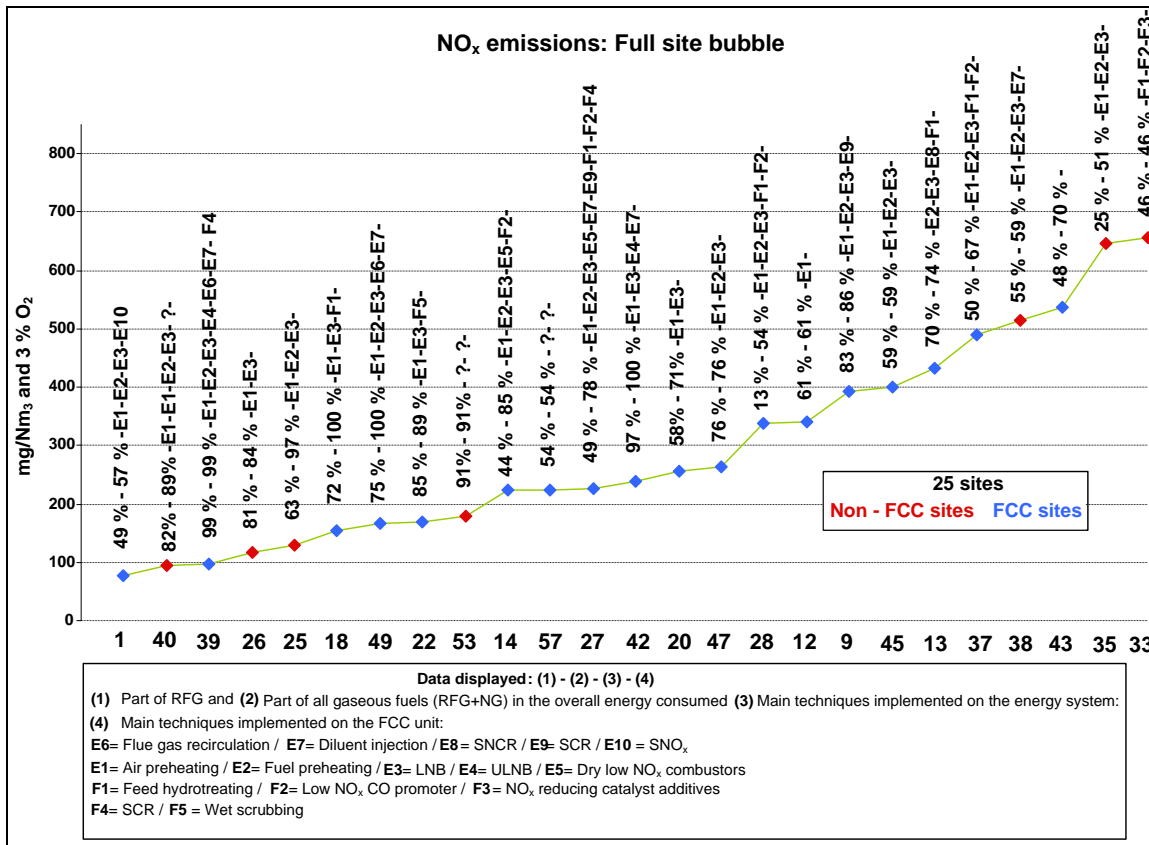


Figure 3.17: Equivalent concentration of the NO_x emissions from the whole energy system, FCC and SRU units of 25 European refineries

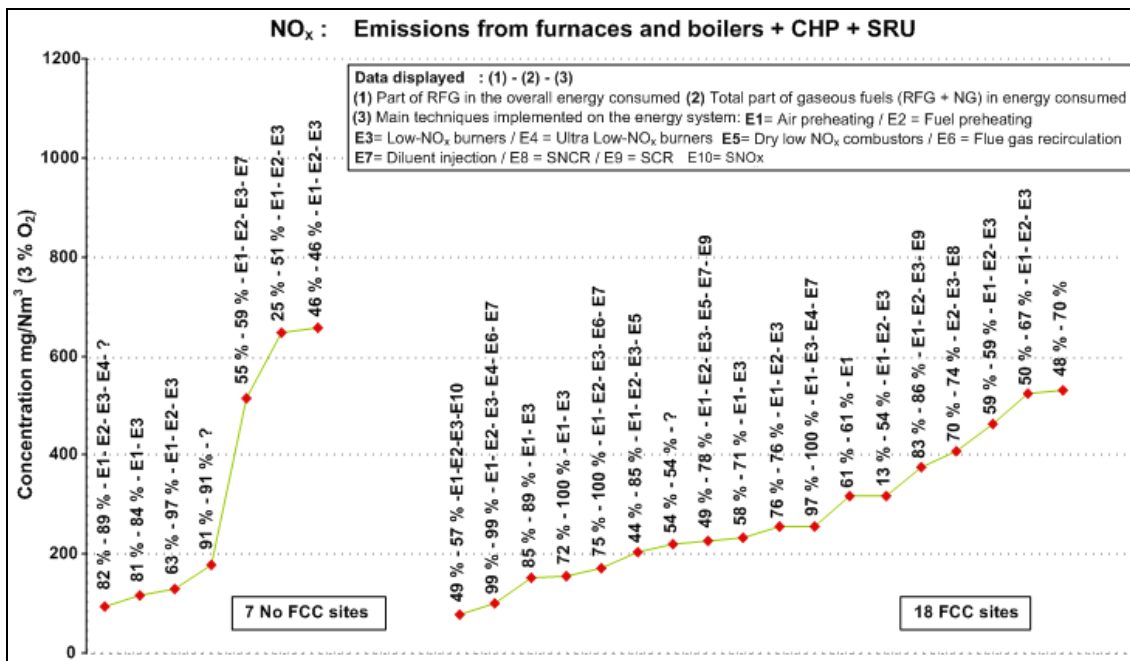


Figure 3.18: Equivalent concentration of the NO_x emissions from the whole energy system and the FCC unit of 30 European refineries

Actual SO₂ emissions from European refineries: a bubble-expressed example

Similar to what has been presented above for the NO_x emissions, individual site sets of SO₂ data collected by the TWG have been gathered in Table 3.14. These data have been processed in order to calculate the annual average equivalent concentration of SO₂ in the sum of the flue-

gases emitted by the four categories of contributing units as listed below. These calculations are based on actual emissions reported for the year 2007 or 2008.

An example of bubble-expressed emission levels is displayed in Figure 3.19, which corresponds to Column (e) in Table 3.14. The full selection of contributors has been used, which includes:

- furnaces and boilers
- CHPs and gas turbines
- FCC units
- sulphur recovery units.

Mass and volumetric contribution terms from each of these four categories were fully available for a sample of 29 sites, of which 10 were non-FCC sites and 19 were FCC sites, and Figure 3.19 shows the range of equivalent concentrations obtained. The contributing unit category for which the data were available, in particular as far as volumetric contributions were concerned, was once again SRUs, mainly responsible for the limitation of this refinery data-set.

As shown in Figure 3.19, an information summary is provided for each refinery on the part taken by the refinery fuel gas and an eventual additional natural gas supply in the refinery energy mix, together with the main NO_x abatement techniques implemented on the FCC unit and the energy system.

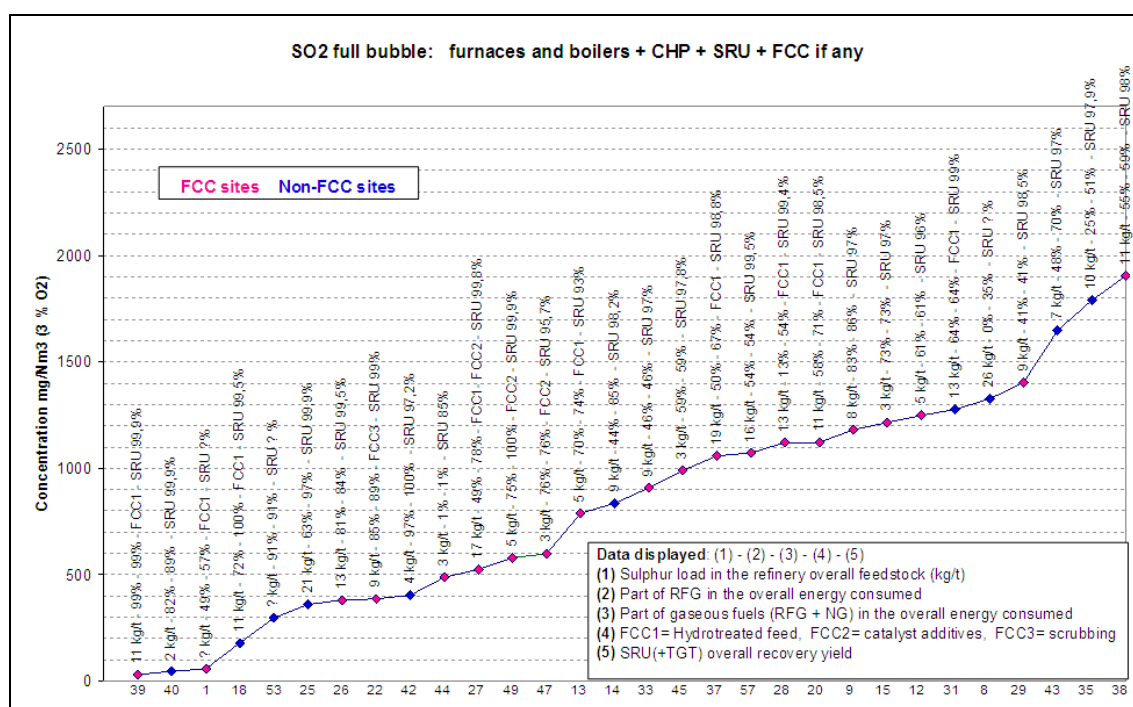


Figure 3.19: Equivalent concentration of the SO₂ emissions from the whole energy system and the FCC and SRU unit of 30 European refineries

Table 3.14: Equivalent concentrations of SO₂ emissions for a sample of European refineries

| questionnaire | Configuration with FCC? | Furnaces+boilers | | CHP+gas turbines | | FCC | | SRU | | Bubble CP (a) | Bubble CP+CHP (b) | Bubble CP+CHP+SRU(c) | Bubble CP+CHP+SRU+ FCC if any (d) | Bubble CP+CHP 'enriched' SRU ^(e) | Bubble CP+CHP+SRU 'enriched' SRU ^(e) |
|-------------------------|-------------------------|------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|-----------------------------------|---|---|
| | | yes=1 | SO ₂ (t) | GNm ³ /yr | SO ₂ (t) | GNm ³ /yr | SO ₂ (t) | GNm ³ /yr | SO ₂ (t) | GNm ³ /yr | mg/N m ³ | mg/N m ³ | mg/N m ³ | mg/N m ³ | mg/N m ³ |
| 53 | 0 | 50 | 2.09 | 0 | 0.00 | - | - | 575 | 0.02 | 24 | 24 | 296 | 296 | 299 | 299 |
| 40 | 0 | 158 | 3.48 | 0 | 0.00 | - | - | 4 | 0.09 | 46 | 46 | 45 | 45 | 47 | 47 |
| 25 | 0 | 568 | 2.16 | 0 | 0.00 | - | - | 244 | 0.10 | 263 | 263 | 360 | 360 | 376 | 376 |
| 26 | 0 | 2639 | 6.15 | 289 | 1.51 | - | - | 5 | 0.06 | 429 | 382 | 380 | 380 | 383 | 383 |
| 44 | 0 | 429 | 0.88 | 0 | 0.00 | - | - | NA | NA | 487 | 487 | 487 | 487 | 487 | 487 |
| 33 | 0 | 1746 | 1.73 | 188 | 0.86 | - | - | 452 | 0.03 | 1007 | 745 | 908 | 908 | 919 | 919 |
| 8 | 0 | 2918 | 2.20 | 0 | 0.00 | - | - | NA | NA | 1326 | 1326 | 1326 | 1326 | 1326 | 1326 |
| 56 | 0 | 3603 | 2.64 | 1351 | 0.98 | - | - | NA | NA | 1365 | 1369 | NA | NA | NA | NA |
| 29 | 0 | 9637 | 6.86 | NA | NA | - | - | 0 | 0.003 | 1405 | 1405 | 1404 | 1404 | 1405 | 1405 |
| 38 | 0 | 9737 | 4.73 | 80 | 1.32 | - | - | 2006 | 0.16 | 2059 | 1623 | 1905 | 1905 | 1954 | 1954 |
| 35 | 0 | 3980 | 1.75 | 2 | 0.27 | - | - | 278 | 0.35 | 2269 | 1963 | 1790 | 1790 | 2100 | 2100 |
| 39 | 1 | 38 | 6.03 | 0 | 0.00 | 68 | 0.73 | 102 | 0.19 | 6 | 6 | 23 | 30 | 23 | 31 |
| 1 | 1 | 23 | 3.03 | 454 | 5.61 | 62 | 0.76 | NA | NA | 8 | 55 | 55 | 57 | 55 | 57 |
| 42 | 1 | 113 | 4.74 | 154 | 0.56 | 970 | 1.13 | 1535 | 0.06 | 24 | 22 | 308 | 404 | 311 | 407 |
| 28 | 1 | 258 | 5.45 | 18044 | 11.58 | 640 | 0.85 | 1498 | 0.34 | 47 | 1075 | 1140 | 1122 | 1163 | 1143 |
| 18 | 1 | 304 | 6.20 | 0 | 0.00 | 42 | 0.84 | 941 | 0.11 | 49 | 49 | 197 | 180 | 201 | 183 |
| 49 | 1 | 1400 | 5.60 | NA | 0.60 | 3200 | 2.00 | 200 | 0.08 | 250 | 226 | 255 | 580 | 258 | 585 |
| 45 | 1 | 1110 | 3.68 | 5800 | 3.71 | 3600 | 3.95 | 760 | 0.05 | 302 | 935 | 1031 | 989 | 1038 | 994 |
| 22 | 1 | 1621 | 4.25 | 131 | 5.95 | 1110 | 1.74 | 1802 | 0.14 | 381 | 172 | 344 | 386 | 348 | 391 |
| 47 | 1 | 3061 | 7.81 | 0 | 0.00 | 1712 | 1.98 | 1096 | 0.02 | 392 | 392 | 531 | 598 | 532 | 599 |
| 36 | 1 | 3470 | 8.24 | 241 | 2.62 | 941 | 1.40 | 2018 | NA | 421 | 342 | NA | NA | 528 | 544 |
| 46 | 1 | 1784 | 4.00 | 0 | 0.66 | 1929 | 1.70 | 1331 | NA | 446 | 383 | NA | NA | 668 | 793 |
| 13 | 1 | 1591 | 3.39 | 0 | 0.00 | 602 | 1.24 | 1527 | 0.08 | 469 | 469 | 897 | 788 | 919 | 802 |
| 7 | 1 | 733 | 1.54 | 0 | NA | 658 | 0.38 | 943 | 0.05 | 476 | NA | NA | NA | NA | NA |
| 57 | 1 | 2781 | 5.61 | 0 | 0.00 | 2243 | 0.90 | 2142 | 0.17 | 496 | 496 | 852 | 1072 | 878 | 1100 |
| 20 | 1 | 3537 | 6.40 | 2 | 3.10 | 4911 | 1.90 | 976 | 0.10 | 553 | 553 | 694 | 1122 | 705 | 1135 |
| 9 | 1 | 1560 | 2.26 | 0 | 0.06 | 986 | 0.70 | 1688 | 0.03 | 689 | 545 | 1124 | 1181 | 1136 | 1191 |
| 27 | 1 | 8337 | 11.91 | 32 | 7.58 | 2630 | 1.43 | 312 | 0.65 | 700 | 429 | 431 | 524 | 445 | 541 |
| 31 | 1 | 5098 | 6.07 | 143 | 1.87 | 896 | 1.09 | 5710 | 0.23 | 839 | 659 | 1338 | 1278 | 1378 | 1311 |
| 14 | 1 | 9475 | 10.12 | 0 | 5.55 | 2121 | 0.94 | 2604 | 0.37 | 936 | 605 | 753 | 836 | 771 | 855 |
| 37 | 1 | 4706 | 4.85 | 0 | 1.79 | 303 | 1.25 | 3430 | 0.08 | 970 | 708 | 1210 | 1058 | 1225 | 1069 |
| 12 | 1 | 5903 | 5.03 | 0 | 0.00 | 1652 | 1.31 | 421 | 0.05 | 1174 | 1174 | 1245 | 1248 | 1257 | 1258 |
| 43 | 1 | 9218 | 7.20 | 194 | 1.00 | 3779 | 2.51 | 4632 | 0.10 | 1280 | 1148 | 1692 | 1649 | 1713 | 1664 |
| 32 | 1 | 4193 | 3.13 | 3 | 1.15 | 708 | 0.71 | 340 | NA | 1340 | 980 | NA | NA | 1060 | 1051 |
| 15 | 1 | 1328 | 0.75 | 0 | 0.00 | 543 | 1.21 | 583 | 0.06 | 1760 | 1760 | 2351 | 1215 | 2533 | 1251 |
| Number of values | | 35 | 35 | 32 | 32 | 24 | 24 | 33 | 30 | 35 | 34 | 30 | 20 ⁽¹⁾ | 33 | 23 ⁽¹⁾ |
| Average | | 3060 | 4.63 | 842 | 1.81 | 1513 | 1.36 | 1217 | 0.13 | 705 | 671 | 846 | 816 ⁽¹⁾ | 862 | 824 ⁽¹⁾ |
| Min. value | | 23 | 0.75 | 0 | 0.00 | 42 | 0.38 | 0 | 0.00 | 6 | 6 | 23 | 30 ⁽¹⁾ | 23 | 31 ⁽¹⁾ |
| 5th perc. | | 46 | 1.34 | 0 | 0.00 | 63 | 0.70 | 0 | 0.00 | 19 | 23 | 50 | 56 ⁽¹⁾ | 52 | 70 ⁽¹⁾ |
| 50th perc. | | 1784 | 4.73 | 0 | 0.76 | 978 | 1.23 | 941 | 0.08 | 487 | 521 | 802 | 913 ⁽¹⁾ | 771 | 855 ⁽¹⁾ |
| 95th perc. | | 9524 | 8.80 | 3553 | 6.68 | 3752 | 2.43 | 3911 | 0.36 | 1850 | 1671 | 1853 | 1296 ⁽¹⁾ | 2013 | 1306 ⁽¹⁾ |
| Max. value | | 9737 | 11.91 | 18044 | 11.58 | 4911 | 3.95 | 5710 | 0.65 | 2269 | 1963 | 2351 | 1649 ⁽¹⁾ | 2533 | 1664 ⁽¹⁾ |

(a) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers.
(b) Equivalent concentration calculated for off-gases emitted by all furnaces, boilers, and CHP and stand-alone gas turbines if any.
(c) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers, CHP and stand-alone gas turbines if any, and SRUs.
(d) Equivalent concentration corresponding to the sum of (c) and off-gases emitted by the FCC units if any.
(e) Equivalent concentration calculated as for (c) and (d) but neglecting the volumetric contribution from SRUs.
(f) NB: Site 1 data made available for 2009 emissions- tail gas of SRU treated in SNO_x of CHP plant.
NA: data not available to the TWG.
⁽¹⁾ These values are calculated only for the FCC refinery sample.
Source: [TWG data collection questionnaires]

However, flue-gases emitted by sulphur recovery units are typically highly concentrated, representing, at the site level, small volumetric contributions which are rarely measured and often estimated with rather significant uncertainty. As an alternative - which corresponds to Column (f) in Table 3.14 - these small volumetric contributions could be neglected. The equivalent concentration would then be calculated with the mass contributions from the four categories of sources mentioned above, but only divided into the volumetric contributions from:

- furnaces and boilers
- CHPs and gas turbines
- and FCC units.

With this option, data necessary for the calculation are available for a wider sample of 32 sites, of which 10 are non-FCC sites and 22 are FCC sites. The site equivalent concentrations obtained for the whole group of refineries are, on average, slightly higher than those obtained in the first case, due to their artificial 'enrichment' related to the decrease of the overall flue-gas volume.

3.1.3 Emissions to water

Waste waters consist of cooling water, process water, sanitary sewerage water and storm water. The quantity of waste waters generated and their characteristics depend on the process configuration. This can vary over time and can vary from one refinery site to another, depending on refinery complexities, variability of feedstocks, integration with petrochemical facilities, techniques, etc.

Waste waters are generally treated in on-site waste water treatment facilities or sometimes by external Waste Water Treatment Plants (WWTP) and then discharged. Depending on the origin of the waste water, these can be contaminated with hydrocarbons, inorganics, metals and salts that may have the potential to impact the receiving environment. Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia, hydrogen sulphide and hydrocarbons). Sour water needs stripping prior to further treatment or reuse as wash water. When off-gases are generated in this pretreatment step these should be properly routed and treated before release (see Section 4.24.2).

Depending on the prevailing climate and the location's housekeeping, storm or rainwater can also generate a significant effluent stream in refineries. When rainwater comes into contact with potentially oil-polluted surfaces ('surface water run-off'), this requires treatment.

The effect of rainwater on both the amount and the quality of the effluent water and the problems that the water discharges to either fresh continental waters or to the sea are issues to consider. Furthermore, sanitary waste water and firefighting water are waste water streams which need attention and quality control prior to deciding on treatment, direct discharge and/or potential reuse.

The water effluent quality parameters to be considered relevant for refining activities are mainly the pH, total suspended solids (TSS), total organic carbon (TOC) or COD, total nitrogen and its various forms (organic R-NH₂, ammonium NH₄⁺, reduced or Kjeldahl NTK, nitrite NO₂, and nitrate NO₃), total phosphorus, BOD, Total Petroleum Hydrocarbons (TPH), aromatics (BTEX), phenols, PAH, metals, temperature. Based on the data collected (see Section 3.1.1.2), an average of 5 – 6 m³ is used (process waste water, cooling water and sanitary waste water) per tonne of feed. This value is strongly dependent on the type of cooling system in use on site, driving the level of water recycling. Water from processes account for around 0.1 – 1.6 m³/tonne of feed (see Section 3.24).

The resulting discharge of the aforementioned substances depends on the ‘in-process’ preventive measures (knowledge of all streams, reduction at source, good housekeeping, reuse) and the presence and technical standards of waste water treatment facilities. The typical process water pollutants and/or waste water parameters relevant to the overall refining process and prior to any purification steps are as stated in Table 3.15.

Table 3.15: Representative concentrations of pollutants in typical refinery effluents before treatment

| Source | Oil | H ₂ S (RSH) | NH ₃ (NH ₄ ⁺) | Phenols | BOD COD TOC | CN ⁻ (CNS ⁻) | TSS |
|--|-------|------------------------|---|---------|-------------------|-------------------------------------|-----|
| Distillation Units | XX | XX | XX | X | XX | - | XX |
| Hydrotreatment | XX | XX(X) | XX(X) | - | X(X) | - | - |
| Visbreaker | XX | XX | XX | XX | XX | X | X |
| Catalytic Cracking | XX | XXX | XXX | XX | XX | X | X |
| Hydrocracking | XX | XXX | XXX | - | X | - | - |
| Lube oil | XX | X | X | - | XX | - | - |
| Spent caustic | XX | XX | - | XXX | XXX | X | X |
| Ballast water | X | - | - | X | X | X | X |
| Utilities (Rain) | - (X) | - | - | - | X | - | - |
| Sanitary/Domestic | - | - | X | - | X | - | XX |
| Key: X = <50 mg/l XX = 50 – 500 mg/l XXX = >500 mg/l | | | | | | | |
| Source: [166, CONCAWE 1999] | | | | | | | |

Table 3.16 summarises the annual average range of the water effluents from European refineries. Most data were gathered in 2009 – 2010 by the Technical Working Group set up for the revision of this document, and relate to a sample of 44 sites, all equipped with a dedicated WWTP. These data reflect an annual period of continuous emissions between the years 2006 and 2008.

The details on the various treatment steps in operation at the refinery sites are shown in Section 4.24.

More detailed data on the main parameters used for characterising organic and nitrogen compounds are shown in Table 3.17 and Table 3.18. The actual range and distribution shape of annual average concentrations and their eventual correlation with related specific emissions are displayed in Figure 3.20 to Figure 3.25, respectively for parameters TOC, COD, BOD₅, TSS and Total Nitrogen. These particular figures only concern data relating to refineries where aqueous effluents are treated in a single dedicated waste water treatment plant.

The amount of oil discharged is usually expressed in grams of Total Hydrocarbon Content (THC) per tonne of refinery throughput. According to CONCAWE, nearly 90 % of the European refineries meet the standard of the Oslo/Paris Commission of 3 grams THC/tonne of refinery throughput since the early 1990s.

Table 3.16: Typical refinery influent/effluent annual average composition and load

| Parameter | Composition after pretreatment by API, CPI and SWS | | Annual effluent composition downstream WWTP | | Specific load (g/t feedstock) | | No ⁽²⁾ | |
|-----------------------------|--|-----------|---|-----------------|-------------------------------|-----------------|-------------------|----|
| | Average | Max. | Min. – Max. | | | | | |
| pH (pH unit) | 7 | 10 | 6 – 9 | | | | | |
| Temperature (°C) | 25 | 45 | 10 – 35 | | | | | |
| | | | 5th – 95th Percentile | 50th Percentile | 5th – 95th Percentile | 50th Percentile | | |
| Concentration in mg/l | TOC | 100 | 250 | 4 – 50 | 14 | 1 – 15 | 5.5 | 22 |
| | COD | 300 – 500 | 1 000 | 19 – 125 | 66 | 9 – 85 | 27.2 | 38 |
| | BOD ₅ | 80 – 150 | 300 | 2 – 30 | 10 | 0.5 – 25 | 4.4 | 31 |
| | HOI ⁽³⁾ | 40 – 50 | 100 | 0.05 – 6.3 | 1.5 | 0.1 – 3 | 0.4 | 15 |
| | HOI ⁽⁴⁾ | NA | NA | 0.3 – 5 | 1.2 | 0.03 – 10 | 0.6 | 11 |
| | TSS | 20 – 60 | 200 | 4 – 35 | 15 | 1 – 30 | 6.3 | 37 |
| | AOX ⁽¹⁾ | NA | NA | 0 – 6 | 0.2 | 0 – 0.5 | 0.06 | 14 |
| | Ammonium-N | 12 – 15 | 30 | 0.3 – 15 | 2.7 | 0.1 – 10 | 1.2 | 19 |
| | Nitrites-N | NA | NA | 0.03 – 1.5 | 0.2 | 0.05 – 0.7 | 0.1 | 13 |
| | Nitrates-N | NA | NA | 0.4 – 12 | 1.7 | 0.2 – 3 | 1.4 | 15 |
| | Kjeldahl nitrogen | 25 | 50 | 2 – 20 | 5.4 | 1 – 6 | 2.3 | 13 |
| | Total Nitrogen | 25 | 50 | 3 – 22 | 8 | 1 – 20 | 4 | 38 |
| | Phosphate | 5 | 20 | 0.1 – 1.5 | 0.3 | 0.05 – 1 | 0.13 | 7 |
| | Total Phosphorus | NA | NA | 0.05 – 4 | 0.6 | 0.05 – 2 | 0.3 | 26 |
| | Anionic agents | NA | NA | 0.2 – 0.3 | 0.25 | 0.1 – 0.2 | 0.15 | 2 |
| | Cyanide ⁽¹⁾ | 0 – 3 | 5 | 0.003 – 0.1 | 0.015 | 0.001 – 0.03 | 0.004 | 16 |
| | Sulphide | 5 | 10 | 0.005 – 0.2 | 0.05 | 0.002 – 0.25 | 0.025 | 16 |
| | Phenols | 12 | 25 | 0.01 – 0.4 | 0.1 | 0.001 – 0.3 | 0.02 | 29 |
| | MTBE ⁽¹⁾ | 0 – 3 | 15 | 0.003 – 0.1 | 0.02 | 0.001 – 0.03 | 0.005 | 3 |
| | Fluoride ⁽¹⁾ | 0 – 30 | 60 | 0.2 – 3 | 0.8 | 0.3 – 2 | 0.6 | 7 |
| | Benzene | NA | 10 | <0.001 – 0.1 | 0.001 | <0.001 – 0.05 | 0.002 | 10 |
| | Toluene | NA | NA | <0.001 – 0.6 | 0.003 | <0.001 – 0.1 | 0.004 | 10 |
| | Ethylbenzene | NA | NA | <0.001 – 0.005 | 0.001 | <0.001 – 0.007 | 0.004 | 9 |
| | Xylenes | NA | NA | <0.001 – 0.2 | 0.001 | <0.001 – 0.15 | 0.004 | 7 |
| | BTEX | 5 | 10 | <0.001 – 1 | 0.005 | <0.001 – 0.2 | 0.01 | 10 |
| | PAH-16 | 0.1 | 0.5 | <0.0001 – 0.01 | 0.0007 | <0.0001 – 0.005 | 0.0003 | 11 |
| | Arsenic-As | NA | NA | <0.001 – 0.02 | 0.003 | <0.001 – 0.02 | 0.0007 | 21 |
| | Boron-B | NA | NA | 0.2 – 0.6 | 0.4 | NA | NA | 4 |
| | Cadmium-Cd | NA | NA | <0.001 – 0.05 | 0.001 | <0.0001 – 0.005 | 0.001 | 18 |
| | Chromium-Cr | NA | 100 | <0.001 – 0.05 | 0.003 | <0.0001 – 0.005 | 0.001 | 23 |
| | Chromium VI | NA | NA | <0.001 – 0.02 | 0.002 | <0.0001 – 0.002 | 0.001 | 7 |
| | Cobalt-Co | NA | NA | <0.001 – 0.003 | 0.001 | NA | NA | 3 |
| | Copper-Cu | NA | NA | 0.01 – 0.1 | 0.05 | <0.001 – 0.03 | 0.002 | 27 |
| Iron-Fe | NA | NA | 0.15 – 3 | 0.4 | 0.01 – 0.6 | 0.15 | 14 | |
| Mercury-Hg | NA | NA | <0.0001 – 0.003 | 0.0002 | <0.0001 – 0.002 | 0.0001 | 21 | |
| Manganese-Mn | NA | NA | 0.02 – 0.5 | 0.08 | 0.001 – 1.8 | 0.04 | 9 | |
| Molybdenum-Mo | NA | NA | 0.004 – 0.02 | 0.01 | NA | NA | 4 | |
| Nickel-N | NA | NA | 0.002 – 0.1 | 0.01 | <0.001 – 0.03 | 0.006 | 22 | |
| Lead-Pb | NA | 10 | <0.0001 – 0.01 | 0.001 | <0.0001 – 0.02 | 0.005 | 25 | |
| Selenium-Se | NA | NA | 0.003 – 0.08 | 0.04 | NA | NA | 5 | |
| Stain-Sn | NA | NA | <0.001 – 0.02 | 0.01 | <0.0005 – 0.005 | 0.004 | 6 | |
| Vanadium-V | NA | NA | 0.005 – 0.1 | 0.02 | <0.001 – 0.01 | 0.003 | 10 | |
| Zinc-Zn | NA | NA | 0.005 – 0.12 | 0.03 | <0.001 – 0.1 | 0.015 | 29 | |
| Heavy metals ⁽⁵⁾ | 1 | 2 | 0.05 – 1.0 | 0.2 | 0.02 – 2 | 0.1 | - | |

(¹) Dependent on whether or not relevant units are part of the refinery.
(²) Number of available site yearly concentration values provided to the TWG.
(³) Hydrocarbon Oil Index measured according to method EN 9377-1.
(⁴) Hydrocarbon Oil Index measured according to method EN 9377-2:2000 (GC-FID).
(⁵) Sum of individual percentile data for the following metals: Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn; V, Zn.
(-) Not appropriate.
Source: [TWG data collection questionnaires]

Table 3.17: Emissions of main organic pollutants and suspended solids from a sample of 48 European sites

| Site label | Total feed refined kt | Dedicated WWTP yes=1 | TOC | | | BOD ₅ | | | COD | | | TSS | | |
|--------------------------------|--------------------------|----------------------------|------|-------|----------|------------------|------|---------|-------|-------|---------|-----|-------|---------|
| | | | mg/l | g/t | kg/yr | mg/l | g/t | kg/yr | mg/l | g/t | kg/yr | raw | final | kg/yr |
| 38 | 8 183 | 0 | 50.0 | 5.4 | 44 000 | 60 | 6.5 | 53 000 | 170 | 18.3 | 150 000 | | 49.0 | 43 000 |
| 1 | 9 096 | 0 | 10 | 7.4 | 67 000 | 5 | 3.9 | 35 510 | 28 | 20.3 | 184 920 | | | |
| 6 | 12 400 | 0 | | | | | | | | 21.5 | 266 897 | | | |
| 26 | 10 193 | 0 | | | | 14 | 7.8 | 79 967 | 115 | 54.3 | 553 019 | 71 | 62.8 | 350 232 |
| 58 | 11 430 | 0 | | | | | 6.9 | 78 937 | | 61.3 | 700 976 | | | 157 515 |
| 30 | 10 490 | 0 | | | | 102 | 16.9 | 176 843 | 374 | 61.7 | 647 501 | | 72.8 | 125 970 |
| 27 | 19 151 | 0 | | | | 15 | | | 115 | | | 200 | 25.0 | |
| 31 | 12 087 | 0 | 29.2 | 10.6 | 128 406 | | | | | | | 127 | 76.9 | 377 678 |
| 48 | 6 900 | 0 | | 94.6 | 652 522 | | | | | | | | | |
| 51 | 4 400 | 0 | | 138.4 | 608 808 | | | | | | | | | |
| 35 | 3 624 | 1 | 20.4 | 1.3 | 4 630 | 8 | 0.5 | 1 774 | 74 | 4.6 | 16 771 | | 14.2 | 3 211 |
| 56 | 6 276 | 1 | 20.6 | 2.4 | 14 919 | 4 | 0.4 | 2 818 | 55 | 6.3 | 39 701 | 56 | 8.6 | 6 235 |
| 11 | 9 350 | 1 | | | | 13 | 2.2 | 20 983 | | 9.1 | 84 684 | | 7.3 | 11 571 |
| 39 | 10 098 | 1 | 9.0 | 2.5 | 25 600 | 3 | 0.9 | 9 000 | 33 | 9.3 | 94 000 | 9 | 9.0 | 25 600 |
| 40 | 5 668 | 1 | 11.7 | 3.0 | 16 900 | 8 | 2.1 | 11 700 | 42 | 10.6 | 60 000 | 24 | 4.2 | 6 000 |
| 41 | 3 942 | 1 | | | | | 4.3 | 16 900 | | 11.4 | 44 900 | | | 10 800 |
| 4 | 4 900 | 1 | | | | 2 | 0.7 | 3 524 | 37 | 11.5 | 56 397 | | 6.5 | 9 770 |
| 19 | 3 359 | 1 | | | | 31 | 4.4 | 14 782 | 82 | 11.9 | 39 936 | | | |
| 17 | 728 | 1 | | | | 24 | 3.0 | 2 184 | 112 | 13.9 | 10 115 | | 29.7 | 2 679 |
| 47 | 11 871 | 1 | 4.0 | 1.0 | 11 857 | | | | 65 | 14.8 | 175 364 | 72 | 17.0 | 45 043 |
| 15 | 4 858 | 1 | 18.0 | 4.1 | 19 959 | 10 | 2.2 | 10 881 | 88 | 16.5 | 80 365 | 25 | 20.0 | 20 395 |
| 42 | 10 916 | 1 | 22.0 | 5.6 | 61 139 | | | | 66 | 17.1 | 186 463 | 36 | 10.0 | 29 352 |
| 59 | 3 513 | 1 | | | | 9.27 | 1.5 | 5 331 | 95.88 | 18.6 | 65 333 | | 22.6 | 13 007 |
| 12 | 6 412 | 1 | 12.8 | 5.5 | 35 100 | 5 | 2.1 | 13 329 | 44 | 18.8 | 120 274 | | 7.9 | 21 569 |
| 50 | 4 620 | 1 | 12.5 | 5.4 | 25 162 | 27 | 11.6 | 53 508 | 45 | 19.7 | 91 085 | | 17.2 | 34 557 |
| 52 | 4 990 | 1 | 18.1 | 7.6 | 38 000 | | | | 53 | 22.4 | 112 000 | | 4.8 | 10 000 |
| 34 | 10 462 | 1 | 1.3 | 0.5 | 5 293 | | | | | 23.3 | 243 508 | | | |
| 28 | 14 251 | 1 | | | | | | | 55 | 26.2 | 372 765 | 100 | 6.4 | 43 509 |
| 9 | 5 727 | 1 | | | | 2 | 3.2 | 18 300 | 21 | 26.7 | 152 838 | | 8.5 | 61 319 |
| 16 | 7 153 | 1 | 15.2 | 5.6 | 40 020 | 8 | 2.9 | 21 031 | 73 | 27.6 | 197 587 | | 12.0 | 32 967 |
| 46 | 9 712 | 1 | 12.0 | 3.7 | 36 397 | | | | 98 | 29.5 | 286 809 | | 13.0 | 37 792 |
| 36 | 5 622 | 1 | | | | 13 | 6.8 | 38 002 | 59 | 31.4 | 176 436 | | 13.5 | 40 716 |
| 7 | 3 268 | 1 | | | | 4 | 17.9 | 58 390 | 8 | 31.4 | 102 758 | | 6.3 | 86 301 |
| 10 | 8 852 | 1 | | | | 24 | 5.5 | 48 444 | 136 | 31.7 | 280 318 | 80 | 32.0 | 67 095 |
| 22 | 8 635 | 1 | 10.0 | 8.2 | 70 985 | 18 | 14.2 | 122 237 | 41 | 33.0 | 284 850 | | 19.9 | 138 938 |
| 32 | 5 886 | 1 | 46.8 | 14.9 | 87 834 | | | | 111 | 35.4 | 208 325 | 178 | 22.4 | 42 040 |
| 25 | 3 613 | 1 | | | | | | | 48 | 35.9 | 129 597 | | 21.8 | 59 375 |
| 57 | 5 778 | 1 | | | | 8 | 5.6 | 32 318 | 53 | 36.3 | 209 729 | | 23.5 | 92 272 |
| 37 | 7 293 | 1 | | | | | | | 109 | 38.9 | 283 706 | | | |
| 5 | 2 772 | 1 | | | | 6 | 3.5 | 9 800 | 90 | 49.8 | 138 000 | | 14.8 | 22 700 |
| 49 | 15 000 | 1 | | | | 32 | 10.7 | 160 810 | 149 | 49.9 | 748 772 | | 19.0 | 95 481 |
| 13 | 5 303 | 1 | | | | 13 | 8.3 | 43 989 | 76 | 50.1 | 265 582 | | 16.3 | 57 490 |
| 18 | 8 272 | 1 | | | | 13 | 15.3 | 126 700 | 47 | 55.7 | 460 640 | | | |
| 14 | 16 552 | 1 | | | | 14 | 9.1 | 151 450 | 95 | 56.2 | 930 051 | | 10.7 | 104 707 |
| 29 | 3 817 | 1 | 10.7 | 6.9 | 26 213 | 20 | 13.0 | 49 733 | 121 | 77.3 | 295 211 | | 22.2 | 54 387 |
| 8 | 953 | 1 | | | | 25 | 37.7 | 35 939 | 80 | 110.7 | 105 561 | | 14.0 | 18 637 |
| 33 | 4 610 | 1 | 65.5 | 18.6 | 85 800 | | | | | | | | | |
| 53 | | 1 | 16.0 | | 21 000 | 10 | | 12 000 | 40 | | 48 000 | | 15.0 | 36 000 |
| 54 | 10 794 | 1 | 20.3 | 7.7 | 82 706 | | | | | | | | 47.0 | 199 780 |
| 60 | | 1 | 8.2 | | 18 253 | 2.53 | | 5 256 | 40.23 | | 83 353 | | 10.3 | 21 425 |
| 61 | | 1 | 15.0 | | 157 701 | 15 | | 162 733 | 97 | | 1 028 | | 23.3 | 246 |
| No of values | 48 | 51 | 24 | 23 | 26 | 34 | 32 | 35 | 41 | 42 | 45 | 12 | 39.0 | 41 |
| 5th percentile ⁽¹⁾ | | | 3.9 | 0.9 | 11 528.8 | 2.4 | 0.8 | 3 100 | 29.4 | 9.2 | 35 263 | 15 | 5.7 | 5 004 |
| 50th percentile ⁽¹⁾ | | | 13.9 | 5.5 | 30 656.5 | 11.3 | 4.3 | 20 983 | 65.0 | 26.7 | 133 799 | 56 | 14.0 | 34 557 |
| 95th percentile ⁽¹⁾ | | | 47.7 | 15.7 | 91 327.4 | 29.7 | 17.2 | 157 066 | 125.2 | 62.5 | 503 860 | 147 | 30.6 | 114 976 |

⁽¹⁾ Only for sites with a dedicated WWTP.

Source: [TWG data collection questionnaires]

Table 3.18: Emissions of nitrogen compounds from a sample of 51 European sites

| Site label | WWTP | Total feed | Ammonium (NH ₄ - N) | | | Nitrites (NO ₂ - N) | | | Nitrates (NO ₃ - N) | | | Nitrogen Kjeldahl | | | Total nitrogen (as N) | | | | | |
|-----------------------------|------|------------|--------------------------------|-------|------------------|--------------------------------|------|-------|--------------------------------|-------|---------|-------------------|--------|--------|-----------------------|--------|-------|------------------|---------|---------|
| | | | (¹) | kt | (²) | mg/l | g/t | kg/yr | mg/l | g/t | kg/yr | mg/l | g/t | kg/yr | mg/l | g/t | kg/yr | (³) | mg/l | g/t |
| 1 | 0 | 9 096 | | 0.9 | | | | | | | | | | | | | | 10.70 | | |
| 6 | 0 | 12 400 | | | | | | | | | | | | | | | | | 6.51 | 80 721 |
| 26 | 0 | 10 193 | | | | | | | | 12.52 | 127 639 | 9.80 | 4.63 | 47 170 | 27 | | | 17.15 | 174 808 | |
| 27 | 0 | 19 151 | | | | | 0.60 | | | 1.60 | | | | 11.00 | | | | 13.00 | | |
| 30 | 0 | 10 490 | | | | | | | | | | | | | | | | 71.00 | 11.71 | 122 856 |
| 31 | 0 | 12 087 | | 7.3 | 2.64 | 31 950 | | | | | | | | | | | | 16.80 | 4.67 | 56 400 |
| 38 | 0 | 8 183 | | 12.0 | 1.34 | 11 000 | | | | 16.00 | 1.71 | 14 000 | | | | | | 24.00 | 2.58 | 21 100 |
| 48 | 0 | 6 900 | | | | | | | | | | | | | | | | | 54.93 | 378 998 |
| 51 | 0 | 4 400 | | | | | | | | | | | | | | | | | 21.02 | 92 483 |
| 58 | 0 | 11 430 | | | | | | | | | | | | | | | | | 17.62 | 201 442 |
| 4 | 1 | 4 900 | | | 0.34 | 1 655 | | | | | | | | | | | | | 1.23 | 6 030 |
| 5 | 1 | 2 772 | | | | | | | | | | | | | | | | | 1.84 | 5 100 |
| 7 | 1 | 3 268 | | | | | | | | | | | | | | 21 | 4.50 | 18.67 | 61 017 | |
| 8 | 1 | 953 | | | | | 0.20 | 0.34 | 320 | 1.40 | 1.95 | 1 858 | 3.40 | 4.56 | 4 343 | | | 4.90 | 6.84 | 6 521 |
| 9 | 1 | 5 727 | | | | | | | | | | | | | | | | 3.57 | 4.58 | 26 248 |
| 10 | 1 | 8 852 | | | | | | | | | | | | 30.00 | 6.99 | 61 877 | | | | |
| 11 | 1 | 9 350 | | | | | | | | | | | | | 0.98 | 9 158 | | | | |
| 12 | 1 | 6 412 | | | | | | | | | | | | 5.40 | 2.28 | 14 590 | | | | |
| 13 | 1 | 5 303 | | | | | | | | | | | | | | | | 23.18 | 15.62 | 82 859 |
| 14 | 1 | 16 552 | | | | | | | | | | | | | | | | 8.10 | 4.80 | 79 500 |
| 15 | 1 | 4 858 | 11 | 6.19 | | | 0.60 | | | 7.00 | | | | 13.00 | | 21 | 17.00 | 4.11 | 19 960 | |
| 16 | 1 | 7 153 | | | | | 0.58 | 0.73 | 1 597 | 3.77 | 6.31 | 10 192 | | | | | | 11.20 | 4.08 | 29 215 |
| 17 | 1 | 728 | | | | | | | | | | | | | | | | | 4.02 | 2 930 |
| 18 | 1 | 8 272 | 7 | 0.9 | 1.10 | 9 096 | 0.09 | 0.11 | 910 | 0.60 | 0.71 | 5 846 | | | | | | 1.42 | 1.64 | 13 563 |
| 19 | 1 | 3 359 | | 14.8 | 2.28 | 7 669 | | | | | | | | | | | | | | |
| 22 | 1 | 8 635 | | 1.7 | 1.37 | 11 838 | 0.05 | 0.04 | 349 | 2.40 | 1.91 | 16 536 | | | | | | 5.40 | 4.35 | 37 601 |
| 25 | 1 | 3 613 | | 4.2 | 2.75 | 9 945 | 0.08 | 0.06 | 220 | 0.34 | 0.24 | 854 | | | | | | | | |
| 28 | 1 | 14 251 | 4 | 0. | 0.41 | 5 805 | | | | 0.80 | 0.38 | 5 438 | | | | 9 | 2.20 | 1.09 | 15 541 | |
| 29 | 1 | 3 817 | | | | | 0.00 | | | 1.70 | | | | 4.30 | | | | 6.60 | 3.27 | 12 494 |
| 32 | 1 | 5 886 | | 16.8 | 5.36 | 31 530 | | | | | | | | | | | | 18.90 | 6.03 | 35 472 |
| 33 | 1 | 4 610 | | | | | | | | | | | | | | | | | 49.24 | 227 000 |
| 34 | 1 | 10 462 | | | 1.66 | 17 371 | | | | | 2.60 | 27 239 | 5.20 | | | | | | | |
| 35 | 1 | 3 624 | | 2.7 | 0.17 | 615 | | | | | | | | | | | | | 2.39 | 8 660 |
| 36 | 1 | 5 622 | 15 | 2.7 | | | | | | | | | | | | | | | | |
| 37 | 1 | 7 293 | | | | | | | | | | | | | | | | 9.80 | 3.50 | 25 508 |
| 39 | 1 | 10 098 | 5 | 0.5 | 0.14 | 1 400 | | | | | | | | | | 8 | 1.60 | 0.45 | 4 500 | |
| 40 | 1 | 5 668 | | 2.5 | 0.58 | 3 300 | | | | | | | | | | | | 4.00 | 1.01 | 5 700 |
| 41 | 1 | 3 942 | | | 0.46 | 1 800 | | | 400 | | 1.24 | 4 900 | | | | | | | 2.82 | 11 100 |
| 42 | 1 | 10 916 | 23 | 0.4 | 0.10 | 1 037 | | | | | | | | | | | 43 | 19.50 | 5.04 | 55 000 |
| 46 | 1 | 9 712 | | 4.2 | 1.25 | 12 108 | | | | | | | | | | | | | | |
| 47 | 1 | 11 871 | | | | | | | | | | | | | | | 19 | 5.00 | 0.98 | 11 596 |
| 49 | 1 | 15 000 | | | | | 0.12 | 0.07 | 1 060 | 0.49 | 0.16 | 2 467 | 16.70 | 5.59 | 83 823 | | | 18.32 | 5.47 | 82 064 |
| 50 | 1 | 4 620 | | | | | 2.24 | 3.13 | 4 402 | 5.95 | 11.80 | 12 261 | 5.21 | 2.25 | 10 385 | | | 13.42 | 5.51 | 25 452 |
| 52 | 1 | 4 990 | 32 | 2.7 | | | | | | | | | | | | | | 6.00 | 2.00 | 10 000 |
| 53 | 1 | | 2 | 0.04 | | 50 | | | | | | | | | | 40 | 15.00 | | | 18 000 |
| 54 | 1 | 10 794 | | 7.5 | 2.87 | 30 991 | | | | | | | | | | | | 9.10 | 3.51 | 37 851 |
| 56 | 1 | 6 276 | | | | | | | | | | | | | | | | 4.00 | 0.45 | 2 837 |
| 57 | 1 | 5 778 | | | 5.59 | 32 318 | | | | | | | | | | | | | 5.88 | 33 955 |
| 59 | 1 | 3 513 | | 4.58 | 0.75 | 2 635 | 0.51 | 0.08 | 291.7 | 20.51 | 3.36 | 11 789 | 8.12 | 1.33 | 4 666 | | | 27.96 | 4.80 | 16 856 |
| 60 | 1 | | | 1.45 | | 2 995 | 0.12 | | | 238.5 | 5.44 | | 11 275 | 2.98 | | 6 171 | | | 8.13 | 16 944 |
| 61 | 1 | | | 8.95 | | 94 475 | 0.88 | | 9 277 | 1.00 | | 10 508 | 13.04 | | 624.5 | | | 13.87 | | 146 349 |
| No | 51 | 48 | 8 | 22 | 19 | 22 | 13 | 8 | 11 | 15 | 13 | 15 | 13 | 8 | 10 | 8 | 31 | 38 | 41 | |
| Average (³) | | 7 579 | 12 | 4.71 | 1.64 | 14 617 | 0.47 | 0.23 | 1 733 | 4.60 | 2.37 | 17 520 | 9.86 | 3.57 | 24 281 | 23.5 | 12.84 | 8.19 | 56 152 | |
| 5th perc. (³) | | 2 499 | 2 | 0.36 | 0.13 | 587 | 0.03 | 0.05 | 229 | 0.43 | 0.20 | 1 456 | 3.19 | 1.08 | 2 112 | 8.24 | 1.75 | 0.69 | 3 872 | |
| 50th perc. (³) | | 5 753 | 9 | 2.70 | 1.10 | 6 737 | 0.16 | 0.10 | 400 | 1.70 | 1.42 | 10 192 | 5.40 | 2.28 | 9 158 | 21.2 | 8.12 | 4.05 | 18 000 | |
| 95th perc. (³) | | 14 363 | 29 | 15.00 | 5.40 | 35 426 | 1.49 | 0.74 | 6 840 | 12.40 | 3.00 | 20 817 | 20.35 | 6.57 | 75 045 | 42.1 | 22.26 | 17.30 | 108 255 | |

(¹): 0 = collective, 1 = dedicated. (²): intermediate concentration (in mg/l) after API, CPI and SWS. (³): only for dedicated WWTP.

Source: [TWG data collection questionnaires]

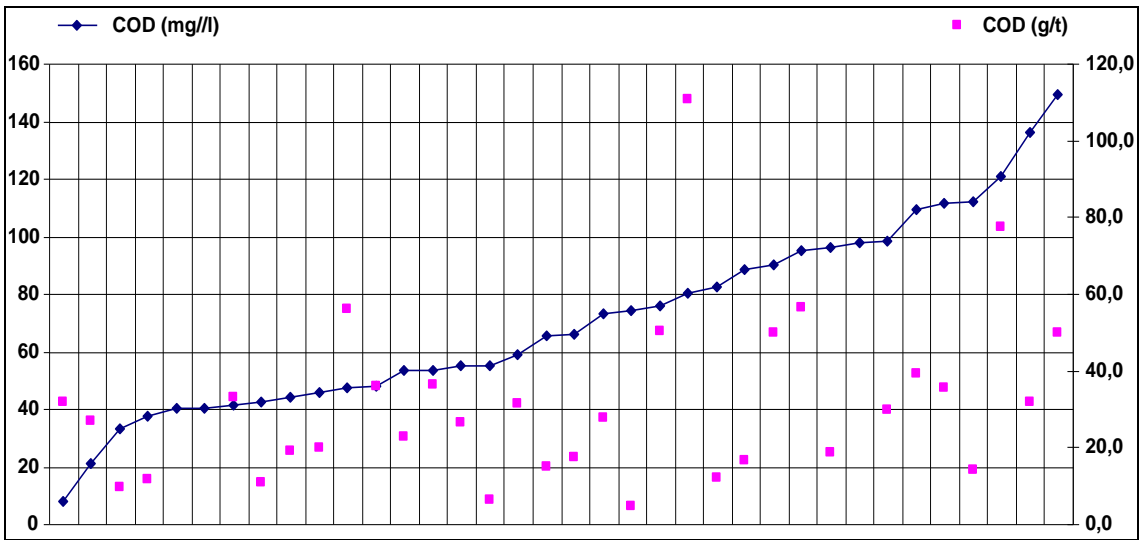


Figure 3.20: Distribution of COD emissions for a sample of 36 European refineries

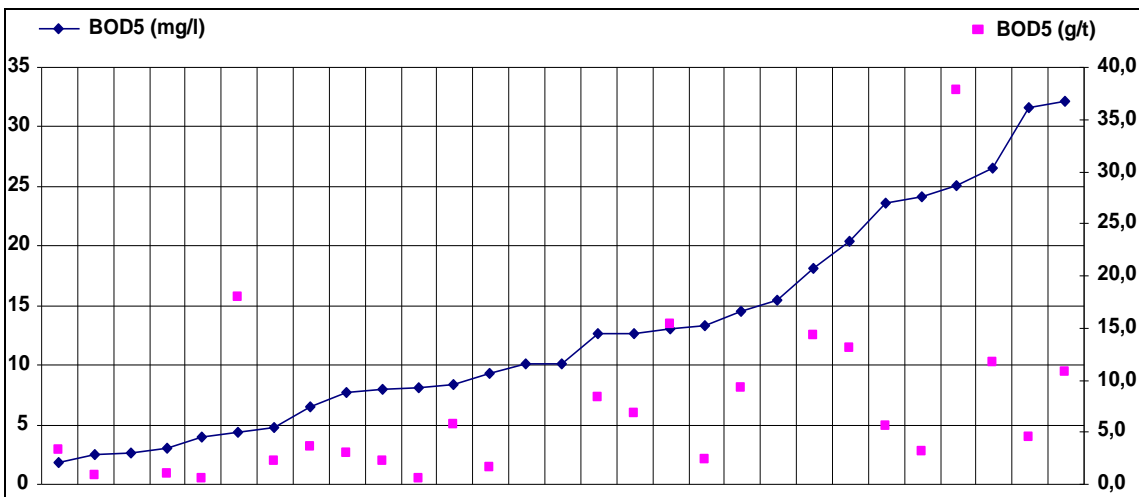


Figure 3.21: Distribution of BOD₅ emissions for a sample of 29 European refineries

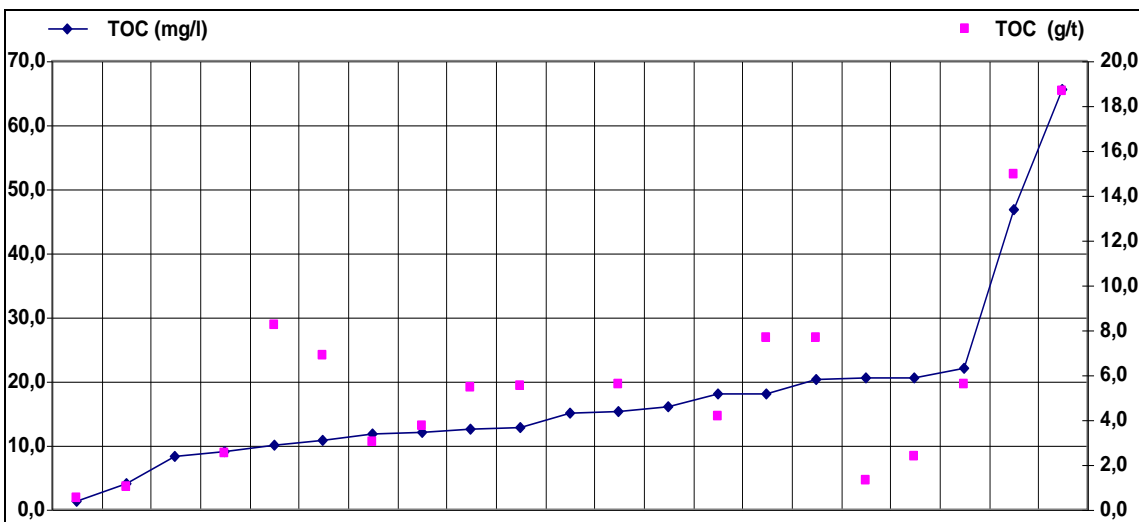


Figure 3.22: Distribution of TOC emissions for a sample of 21 European refineries

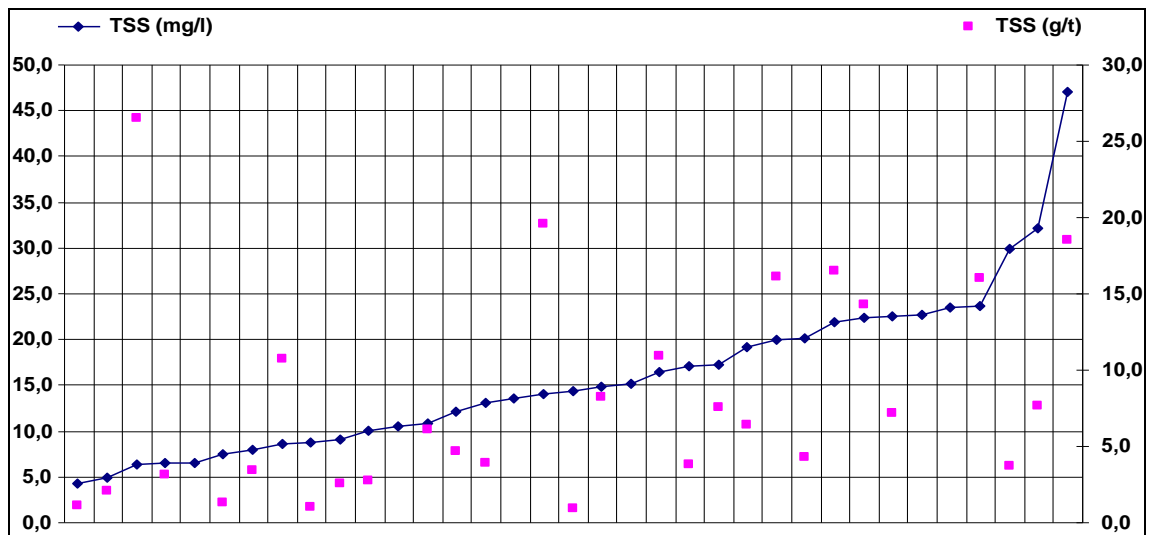


Figure 3.23: Distribution of suspended solid emissions for a sample of 34 European refineries

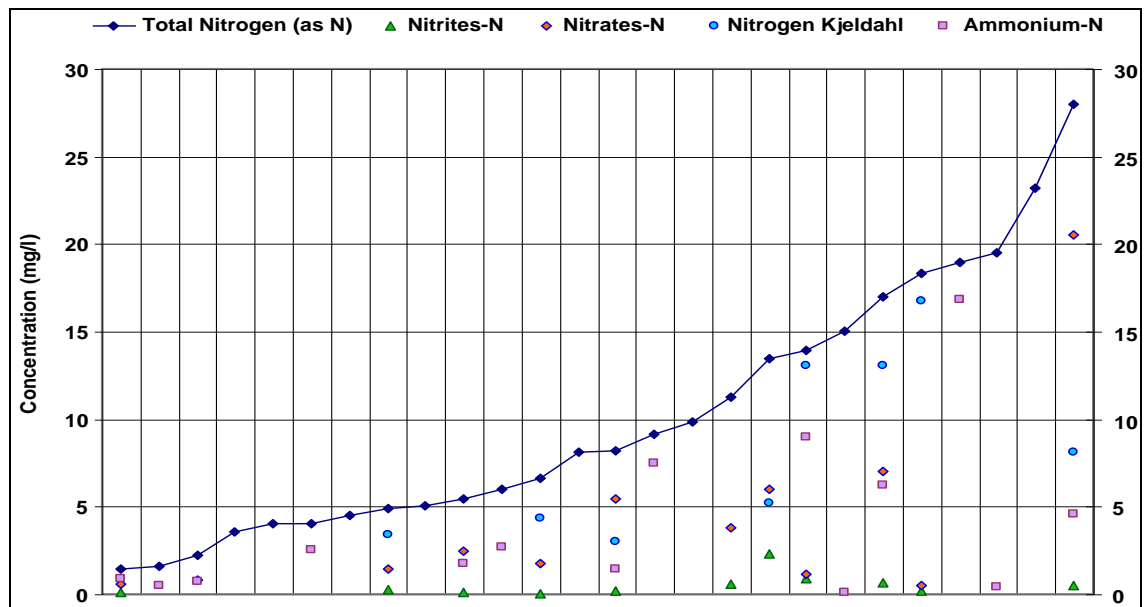


Figure 3.24: Distribution of annual average concentrations of nitrogen compound discharges for a sample of 26 European refineries

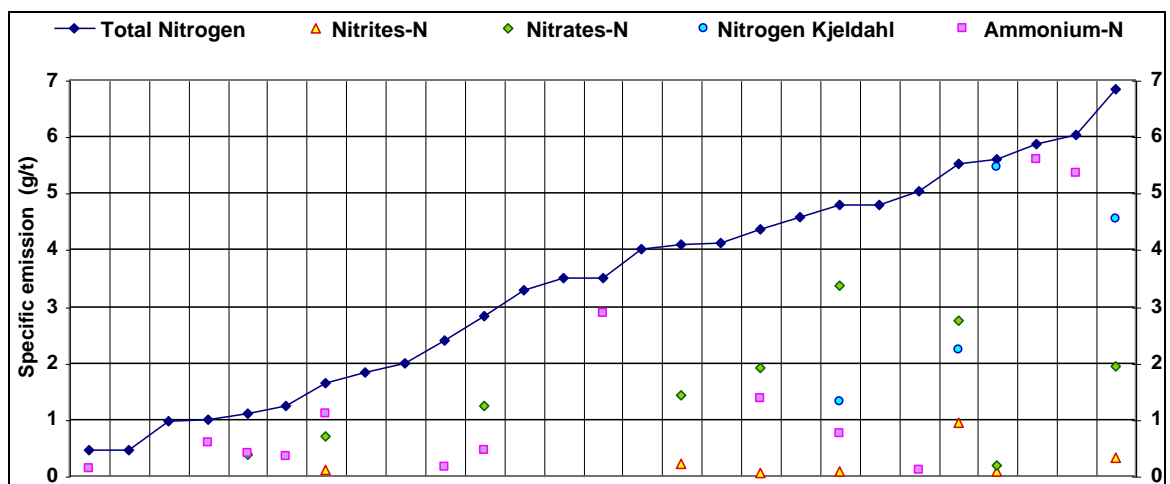


Figure 3.25: Distribution of specific emissions of nitrogen compounds for a sample of 27 European refineries

3.2 Alkylation

This section contains data on consumption and emissions generated by alkylation processes.

Consumption

Table 3.19 gives a summary of the utilities and chemical consumption in the two techniques currently used in the alkylation processes, and for the new solid-acid process.

Table 3.19: Estimated utilities and chemical consumption for the various alkylation techniques

| Values per tonne of alkylate produced | Sulphuric acid | Hydrofluoric | Solid acid |
|--|----------------|---------------|--------------|
| Utilities | | | |
| Electricity (kWh) | 80 – 130 | 20 – 65 | 134 |
| Fuel (MJ) | Not required | 1 000 – 3 000 | Not required |
| Steam (kg) | 815 – 1 200 | 100 – 1 000 | 1 028 |
| Cooling water (m ³) ($\Delta T = 11\text{ }^{\circ}\text{C}$) | 40 – 83 | 62 | 0.78 |
| Industrial water (m ³) | 0.08 | | Not required |
| Chemicals | | | |
| Fresh acid (kg) | 78 – 180 | 1.15 | 0.14 |
| Caustic (as 100 % NaOH) (kg) | 0.41 | 0.57 | Not required |
| Lime | NA | NA | Not required |
| NB: AlCl ₃ and water-free CaCl ₂ consumption depend on operating conditions (water content of feed- and side-reactions). | | | |
| Sources: [175, Meyers 1997], [168, VROM 1999], [204, Canales 2000] | | | |

Emissions

Emissions generated by the alkylation processes are summarised in Table 3.20 to Table 3.22 [161, USAEPA 1995], as reviewed by the TWG.

Table 3.20: Air emissions generated by the alkylation processes

| Air pollutant | Sulphuric acid | Hydrofluoric | Solid acid |
|---|---|--|--|
| CO ₂ , SO ₂ , NO _x and other pollutants from the furnaces(*) | No furnace | From column heating furnaces | No furnace |
| Hydrocarbons | May be released from pressure reliefs, storage, handling operations, spillages and fugitive emissions | | |
| | May be released from water and waste discharges | | No water discharge No waste discharge |
| Halogens | NA | Fluoride compounds may be released from pressure reliefs, vent gas and spillages | No halogens |
| Odours | NA | Acid-soluble oil may be released from process shutdown ponds during maintenance work, particularly the descaling of pipes conveying hydrogen fluoride. This may be odorous | No odour |
| (*) Emissions from these combustion processes are addressed in an integrated way in Section 3.10.3.1. | | | |
| Source: [161, USAEPA 1995] | | | |

Table 3.21: Waste water generated by the alkylation processes

| Water parameter | Sulphuric | Hydrofluoric | Solid acid |
|-----------------|--|---|------------------------|
| Waste water | Waste water produced in the alkylation process may have a low pH if the neutralisation section operates in abnormal conditions, suspended solids, dissolved solids, COD, H ₂ S, and spent acid. | | No liquid waste at all |
| Hydrocarbons | NA | HC from separator drains (surge drum, accumulator, dryer) and spillages, and of acidic effluent containing dissolved and suspended chlorides and fluorides from the settlement pit or the process shutdown ponds. | |
| Acid | Sulphuric acid | Effluents from HF scrubber are 2 – 8 m ³ /h with min./max. compositions of 1 000 – 10 000 ppm F; after lime treatment 10 – 40 ppm F. | |

Table 3.22: Solid waste generated by the alkylation techniques

| Solid waste | Sulphuric | Hydrofluoric | Solid acid |
|--------------------------------------|--|--|---|
| Sludge | NA | The flow 7 – 70 kg sludge per kg used HF (dry solids content 3 – 30 %) | No sludge |
| Hydrocarbons | Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerisation products are removed from the acid as a thick dark oil. | HC from spent molecular sieves, carbon packings and acid-soluble oil. Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerisation products are removed from the acid as a thick dark oil. | No acid-soluble oil - No salts |
| Acid/catalyst products in the sludge | Sludge generated in the neutralisation process contains sulphuric acid. | Inorganic fluorides (Na/KF) and chlorides from treatment stages. Sludge generated in the neutralisation process contains CaF ₂ . | Spent catalyst sent back to supplier for Pt recovery after years of operation |
| Halides | NA | Composition of sludge is 10 – 40 ppm F after lime treatment | No halides |

Source: [161, USAEPA 1995]

3.3 Base oil production

This section gives the consumption and emission values that can be found in the base oil production process identified. It also provides additional information about the nature of substances used in base oil production, in order to highlight the more environmentally significant sub-processes.

Nature of substances used

It is reported that unrefined and mildly refined distillate base oils contain the highest levels of undesirable components, have the largest variation of hydrocarbon molecules; and show the highest potential carcinogenic and mutagenic activities. Highly and severely refined distillate base oils are produced by removing or transforming undesirable components from the unrefined and mildly refined ones. In comparison, the highly and severely refined distillate base oils have a smaller range of hydrocarbon molecules and have demonstrated very low toxicity for mammalian species.

3.3.1 Deasphalting

Consumption

A conventional solvent-based base oil lube complex is energy-intensive. The main reason is the high amount of heat required to evaporate the solvents and to separate them from the raffinate and extract streams. Solvent losses are usually in the order of 1 %, despite extensive solvent recovery. In the tower method, for example, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. It is reported, taking into account the specific input of some crudes and the output of crucial specifications (e.g. CCR), that there is a need to use a higher propane ratio, of up to 9 or 11 to 1.

As an example, the figures below give the utility requirements of solvent deasphalting absorption (SDA) units.

Table 3.23: Consumption data of deasphalting units

| Utility | Data corresponding to 1 000 tonnes of feedstock |
|---|--|
| Fuel | 136 – 150 MWh |
| Power | 12.2 – 21 MW |
| Steam | 166 – 900 tonnes |
| Cooling water | Nil (maximum air cooling) |
| <i>Sources: [175, Meyers 1997], [204, Canales 2000]</i> | |

Table 3.24: Emission data of deasphalting units

| Emissions | | |
|--|--|-------------------------------------|
| Air | Waste water | Solid waste |
| Air emissions may arise from fugitive solvent emissions and process vents. Heater stack gas | The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Oil components | Little or no solid waste generated. |

3.3.2 Aromatic extraction

Consumption

As an example, the figures below in Table 3.25 and Table 3.26 give the utility requirements and the emissions data of aromatic extraction units.

Table 3.25: Consumption data of aromatic extraction units

| Examples of utilities consumption per m ³ feedstock | | |
|--|-------------|----------------|
| Fuel absorbed | 862 – 1 300 | MJ |
| Electricity | 5 | kWh |
| Steam | 8 | m ³ |
| Water cooling ($\Delta T=14$ °C) | 12.5 | m ³ |
| <i>Source: [183, HP 1998] reviewed by TWG</i> | | |

Table 3.26: Emission data of aromatic extraction units

| Emissions | | |
|---|--|--------------------------------------|
| Air | Waste water | Solid waste |
| Fugitive solvent VOC emissions can come from the furfural and NMP from its storage tanks. Flue-gas from fired heater | The total amount of process water is around 2 – 4 m ³ per tonne of product, containing around 15 – 25 ppm furfural, 10 – 15 ppm NMP. The water stream leaving the fractionator is likely to contain some oil and solvents. | Little or no solid wastes generated. |
| <i>Source: [168, VROM 1999]</i> | | |

3.3.3 High-pressure hydrogenation unit

As an example, the figures below in Table 3.27 provide the utility requirements data of a high-pressure hydrogenation unit.

Table 3.27: Typical utility consumption of a high-pressure hydrogenation unit

| Utilities, typical per kt of feedstock | | |
|---|------|----------------|
| Fuel | 11.5 | t |
| Electricity | 26 | kWh |
| Net steam consumption ⁽¹⁾ | 200 | t |
| Water cooling ($\Delta T=14$ °C) | 110 | m ³ |
| ⁽¹⁾ 50 % is recovered as condensate. | | |

3.3.4 Solvent dewaxing

Consumption

The utility requirements in this process together with the aromatic extractions are given in the table below.

Table 3.28: Typical combined utility consumption of solvent dewaxing and aromatic extraction units

| Fuel (MJ/t) | Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, $\Delta T=10$ °C) |
|--|---------------------|-----------------------|---|
| 1 000 – 1 300 | 60 – 160 | 300 – 800 | 10 – 20 |
| <i>Source: [168, VROM 1999], [204, Canales 2000]</i> | | | |

Table 3.29: Emission data of solvent dewaxing units

| Emissions | | |
|---|---|-------------------------------------|
| Air | Waste water | Solid waste |
| VOCs may arise from solvent vapour extraction from the wax filters as well as fugitive emissions. Fugitive solvent VOC emissions can come from the MEK/toluene from storage tanks. Flue-gas from fired heater | The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Potential releases into water are hydrocarbons, sulphur compounds and organic compounds from spillages and leaks, and organic compounds from process waters from solvent recovery operations. Waste water contains 1 – 3 ppm MEK/toluene | Little or no solid wastes generated |

3.3.5 Hydrofinishing

Consumption

The utility needs for hydrofinishing units are shown in the table below.

Table 3.30: Typical utility consumption of hydrofinishing units

| Fuel (MJ/t) | Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, $\Delta T=10$ °C) |
|-----------------------------------|---------------------|-----------------------|---|
| 300 – 550 | 25 – 40 | 100 – 150 | 5 – 15 |
| <i>Source:</i> [168, VROM 1999] | | | |

Table 3.31: Emission data of hydrofinishing units

| Emissions | | |
|--|---|-------------|
| Air | Waste water | Solid waste |
| Pressure relief valves of the hydrofiner, solvent recovery systems and refrigerant systems. Leakages from flanges, glands and seals on pumps, compressors and valves. | Leakages from flanges, glands and seals on pumps, compressors and valves. | NA |

Reference literature

[76, Hydrocarbon processing 2011], [168, VROM 1999], [183, HP 1998], [204, Canales 2000], [272, US EPA 2003], [274, IARC 1983].

3.4 Bitumen production

Consumption

Bitumen blowing is a very low energy process. Some electricity is required for the air blower, product run down pump, and the overhead condensing system. The electricity utilisation in this process is 15 – 35 kWh/tonne and the steam produced in the process is 100 – 200 kg/tonne. For cooling-water utilisation, it is assumed that an air cooler is used as a condenser. If a direct water quench is applied instead of scrubbing, more water is normally used.

Emissions

Available information has been gathered in Table 3.32.

Table 3.32: Emission data for bitumen production units

| | |
|----------------------------|--|
| Air | <p>Flue-gas from fired heater</p> <p>Flue-gas from the overhead vapours incinerator. The overhead vapours from bitumen production, consisting mainly of light hydrocarbons, N₂, O₂, CO₂ and SO₂, are incinerated at high temperature (~800 °C) to ensure complete destruction of components such as H₂S, CO, complex aldehydes, organic acids, PAH and phenolic, which have a highly unpleasant odour. The flow of the oxidiser overhead is around 0.07 – 0.30 Nm³ air/kg feed.</p> <p>The main problems with bitumen production relate to hydrogen sulphide releases from the distilled residues and sour condensates and gas produced in the blowing process.</p> <p>Hydrocarbons and sulphur compounds may emanate from leakages (particularly from overhead systems) and pressure relief valves and in the form of aerosol-containing liquid droplets from the venting of tanker top-loading operations.</p> |
| Process waste water | <p>Sour water is produced in the oxidiser overhead waste water. Its flow is up to 5 m³/tonne feed and it contains H₂S, oil, aromatics, PAH, sulphuric acid, odorous oxidation products (ketones, aldehydes, fatty acids) and particulates.</p> <p>Other potential releases into water are of hydrocarbons and sulphur compounds from spillages and leakages.</p> |
| Solid waste | <p>Slop oil emulsions are formed in the oxidiser overhead slop oil. It consists of an emulsion of light oil, water and particulates.</p> |

3.5 Catalytic cracking

3.5.1 Consumption

The next table shows the energy and process materials usage in the catalytic crackers.

Table 3.33: Typical utility consumption of catalytic crackers

| Utility | FCC | RCC |
|--|-------------|-------------|
| Fuel (MJ/t) | 120 – 2 000 | 120 – 2 000 |
| Electricity (kWh/t) | 8 – 50 | 2 – 60 |
| Steam consumed (kg/t) | 30 – 90 | 50 – 300 |
| Steam produced (kg/t) | 40 – 60 | 100 – 170 |
| Cooling water (m ³ /t, $\Delta T=17$ °C) | 5 – 20 | 10 – 20 |
| Catalyst make-up (kg/t) | 0.4 – 2.5 | 2 – 4 |
| <i>Sources:</i> [204, Canales 2000], [183, HP 1998], [168, VROM 1999], [175, Meyers 1997], [207, TWG 2001] | | |

Virtually all the heat required in a FCC or a RCC unit is generated in the regenerator.

The catalysts consumed and released to air as emissions depend on the type of product processed and can be silica-alumina substrate carrying rare earth and/or precious metals, or more typically consist of rare-earth exchanged zeolites on alumina matrices and clays.

3.5.2 Emissions

3.5.2.1 Air emissions

Within a refining complex, one of the sources with major potential for atmospheric emissions is the catalytic cracking unit. Air emissions arise principally from the regenerator and are mainly CO, CO₂, NO_x, particulates (mainly catalyst fines including their constitutive heavy metals) and SO₂. The emissions from catalytic crackers are very variable, reflecting the variation of the feedstocks used (nitrogen, sulphur, metal contents), and the regenerator and waste heat boiler operating conditions.

Emissions from a FCC unit can increase over time as the quality of air catalyst mixing in the regenerator deteriorates as a result of wear. For example, internal mechanical damage or equipment wear/erosion could occur towards the end of run of the unit and this could significantly increase all unit emissions of CO, NO_x, SO_x and PM.

As already shown in Section 3.1.2, emissions from a FCC unit can be 10 – 30 % of total refinery SO₂ emissions (see Figure 3.13), 15 – 25 % for NO_x (see Table 3.4) and 30 – 40 % for particulates. However, these figures can be subject to wider variation [163, FWE 1999]. The next table shows a summary of the emission factors and emissions from FCCs.

Table 3.34: Emission data and factors found in catalytic crackers (with and without abatement techniques)

| Emissions | PM | SO _x (as SO ₂) | CO | HC | NO _x (as NO ₂) | Aldehydes | NH ₃ |
|--|---------------|--|--------------|-------|--|-----------|-----------------|
| Emission factors (kg/m ³ of fresh feed) | 0.009 – 0.976 | 0.19 – 1.50 | 0.08 – 39.2 | 0.630 | 0.107 – 0.416 | 0.054 | 0.155 |
| Emission data (mg/Nm ³ at 3 % O ₂) | 15 – 1 600 | 320 – 2 500 | 135 – 66 000 | NA | 180 – 700 | NA | NA |
| NB: Values attainable in continuous operation. Emissions values as half hourly mean values Lower levels in the range are catalytic crackers with abatement techniques. Sources: [172, MRI 1997], [221, Italy 2000], [204, Canales 2000], [167, VDI 2000], [194, Winter 2000], [208, Confuorto 2000] Updated TWG 2010 | | | | | | | |

There is a growing trend in the EU towards processing more residual feedstock in FCC units in response to increasing demand for road transport fuels and a decreasing demand for residual fuels. Residual feedstock brings a higher content of coke precursors, sulphur, nitrogen, Ni and V metals, and aromatics. The increased sulphur load has proportional and related effects on the S content in the coke and thus on SO₂ emissions, if abatement provisions as a consequence of the change are not made. The increased nitrogen load potentially leads to the increased production of NO_x precursor compounds NH₃ and HCN, which may or may not lead to increased actual NO_x emissions, depending on the FCC unit regenerator operations.

Potential consequences of the high metals content include:

- a substantial increase in catalyst consumption and potentially higher regenerator PM losses due to increased catalyst attrition;
- the formation of FeS (from the increased feed Fe content) over the equilibrium catalyst, which is then oxidised to SO₂ and SO₃ in the regenerator, thus increasing the flue-gas SO_x content;
- an increase of NO_x emissions, due to the required antimony additions used to passivate nickel to reduce the production of hydrogen.

Residue catalytic crackers (RCC) mainly use atmospheric residue as feedstock. Hence the Conradson carbon, sulphur content and nitrogen content are higher. Therefore, RCCs are potentially a stronger source of SO_x, NO_x, PM and contaminated catalyst than normal FCCs. However, as a consequence of the type of feedstock used in the RCC, the RCC produces more coke and hence more heat should be removed from the regenerators.

Because the catalytic cracker is a significant emitter of pollution in a refinery, there follows a more detailed analysis by type of pollutant.

Carbon dioxide

Carbon dioxide is generated in the catalyst regeneration train and its load depends on the size.

Table 3.35: Range and examples of emissions of CO₂ from catalytic crackers

| Throughput (kt/yr) | % S in feed | Flue-gas flow (Nm ³ /h at 3 % O ₂) | CO ₂ emission load (t/yr) | Specific CO ₂ emission (kg/t) |
|--|-------------|---|--------------------------------------|--|
| 1 314 | <0.5 | 110 000 | 272 243 | 207 |
| 2 350 | 0.35 | 200 000 | 498 006 | 212 |
| Range of emissions | | | 130 000 – 600 000 | 160 – 220(*) |
| (*) High Conradson carbon feed can lead to increasing CO ₂ emissions. Sources: [194, Winter 2000], [172, MRI 1997] reviewed by TWG | | | | |

Carbon monoxide

Relatively high concentrations of carbon monoxide (CO) can be produced during the regeneration of the catalyst. CO is typically converted to carbon dioxide either in the regenerator (full combustion mode) or further downstream in a carbon monoxide boiler (partial combustion mode).

In the full combustion mode, incomplete combustion can lead to releases of carbon monoxide. CO from units operating in full combustion mode ranges typically between 50 and 1 200 mg/Nm³ (depending on temperature, CO promoter level, size of unit).

In the partial combustion mode, depending on the conditions under which the regenerator is operating, the levels of CO in the regenerator exhaust gases feeding the CO boiler may be in the region of 5 % to 10 %, and levels of CO in the exhaust from the CO boiler can be maintained at less than 100 mg/Nm³, depending on the type of CO boiler used [156, MCG 1991].

Table 3.36: Examples of CO from catalytic crackers

| Throughput (kt/yr) | % S in feed | Flue-gas flow (Nm ³ /h at 3 % O ₂) | CO concentration (mg/Nm ³) | CO emission load (t/yr) | Specific CO emission (kg/t) |
|--------------------|-------------|---|--|-------------------------|-----------------------------|
| 1 314 | 0.5 | 110 000 | 215 – 814 | 558 | 0.43 |
| 2 350 | 0.5 | 200 000 | 125 | 194 | 0.08 |

NB: Data are related to yearly average, 3 % O₂, dry conditions.
Source: [194, Winter 2000]

CO boilers are usually used only in connection with FCCs operating in partial combustion mode with CO concentrations in the flue-gas from 5 % to 10 %. They are not used to further reduce CO emissions from units operating in full combustion mode.

Nitrogen oxides

The wide range in NO_x emissions (levels) from catalytic cracker regenerators (gases) reflects the main effects of different combustion conditions on FCC regenerators or FCC CO boilers, the spread in unit capacities and the coke (feed) nitrogen contents. These depend on crude type and upstream process configuration. NO_x emissions are generated in different ways for the two combustion modes.

In the full combustion mode, key parameters potentially affecting the FCC unit NO_x emissions are:

- uneven regenerator catalyst bed temperature and oxygen profiles and distribution;
- use of a CO combustion promoter containing platinum (contributes to NO_x increase);
- antimony additions, often used for high-metal feed applications.

In the partial combustion mode, key parameters potentially affecting the FCC unit NO_x emissions are (Source: [24, Bruhin et al.2003]):

- The formation of NO_x precursor compounds (HCN and NH₃) from the coke nitrogen, depending upon the CO content. Operating conditions with higher excess CO usually favour the formation of these precursors which react to form NO_x and N₂ in the CO boiler downstream of the regenerator.
- Thermal NO_x generated in the CO boiler and fuel NO_x formed depending upon the nitrogen content of the supplemental fuel, the amount and type of fuel, the burners design and the operating conditions in the CO boiler.

The final stack NO_x emissions for a partial-burn regenerator may be similar to, or even higher than, an equivalent full combustion regenerator. It is typically higher than a full combustion unit operating at low excess O₂ (<2 %). Figure 3.26 displays NO_x yearly average concentrations

achieved in 2007 – 2008 for a sample of 21 European FCC units. When available, summary information is also given on NO_x-reducing techniques that were implemented at these plants (values are expressed in mg/Nm³, dry at 3 % O₂). Lower emission values can be found when the highest NO_x reduction additives rates are applied, or when dedicated end-of-pipe treatment techniques are implemented.

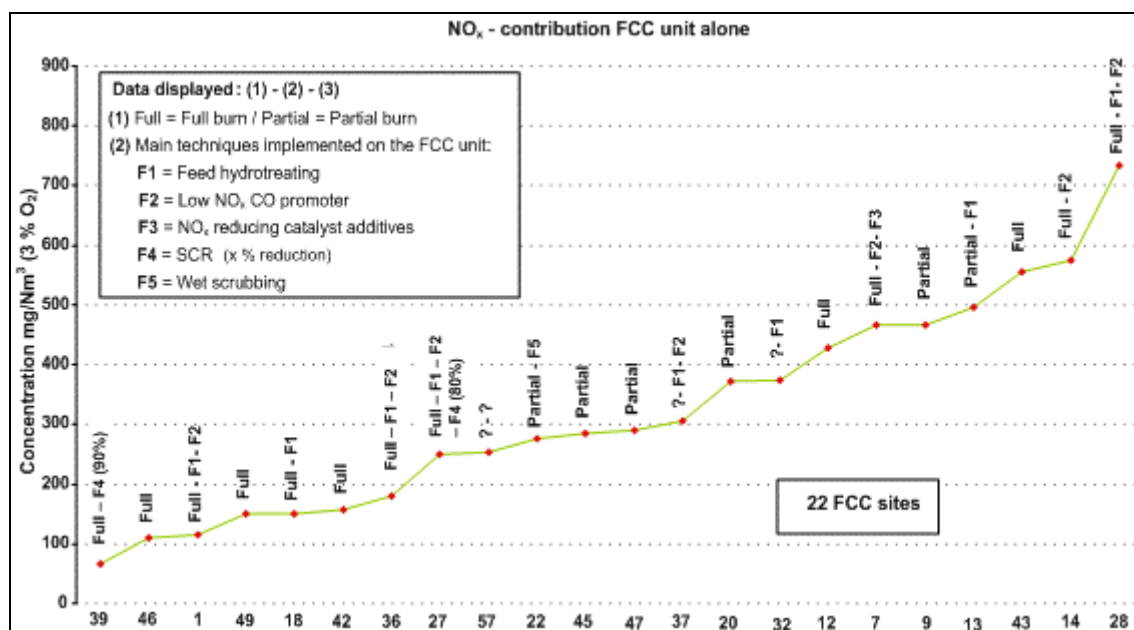


Figure 3.26: NO_x yearly average concentration from a sample of 21 European FCC units

Additional data received for 2009 for a feed hydrotreated (F1) FCC full combustion unit show a yearly average of 116 mg/Nm³ (Source: TWG Austria: Emission declaration for 2009).

According to the CONCAWE 4/09 report, from a nine FCC unit data-set, eight show NO_x emissions under 500 mg/Nm³ and one shows up to 800 mg/Nm³. In the latter case, the unit was using supplementary fuel and firing heavy residue in the CO boiler.

Particulates

Generally a FCC unit is the biggest single emitter of particulates, although the calciner in a coking unit is also a significant emitter. Particulate matter arises from catalyst fines from the catalyst regeneration exhaust gases and catalyst handling and disposal. The emitted catalyst is fine and is produced in a catalytic cracker as a result of the constant movement of the catalyst grains. In the absence of moisture or sulphuric acid condensation, the normal cause of stack plume opacity is the presence of the fine catalyst particles. In practice, operating conditions may have a large effect on particulate emissions. Table 3.37 gives three examples of particulate emissions from catalytic crackers. Lower values in the provided range correspond to FCC equipped with abatement techniques.

Table 3.37: Examples of particulate emissions from catalytic crackers

| Throughput (kt/yr) | Flow (Nm ³ /h at 3 % O ₂) | % S in feed | Concentration (mg/Nm ³) | PM load (t/yr) | Specific emissions ⁽¹⁾ (kg/t) |
|---|--|-------------|-------------------------------------|-----------------------|--|
| 1 314 | 110 000 | 0.5 | 17 | 11.6 | 0.009 |
| 2 350 | 200 000 | 0.5 | 50 | 44.5 | 0.033 |
| 1 750 | NA | NA | 47 | 33.8 | 0.019 |
| Ranges and averages in a sample of 20 European FCC | | | [25 – 189] Avg: 69 | [13 – 340] Avg: 88 | [0.015 – 0.100] Avg: 0.040 |
| ⁽¹⁾ Range and average estimated from FCC capacity. | | | | | |
| Sources: [194, Winter 2000], [172, MRI 1997], [207, TWG 2001], [77, REF TWG 2010] | | | | | |

Figure 3.27 displays the PM yearly average concentrations achieved in 2007 – 2008 for a sample of 20 European FCC units. Where available, summary information is also given on PM-reducing techniques that were implemented at these plants. Values are expressed in mg/Nm^3 , dry at 3 % O_2 . Lower emission values are not necessarily linked with the combustion mode, but are often related with the most advanced ESP or filtering techniques reported.

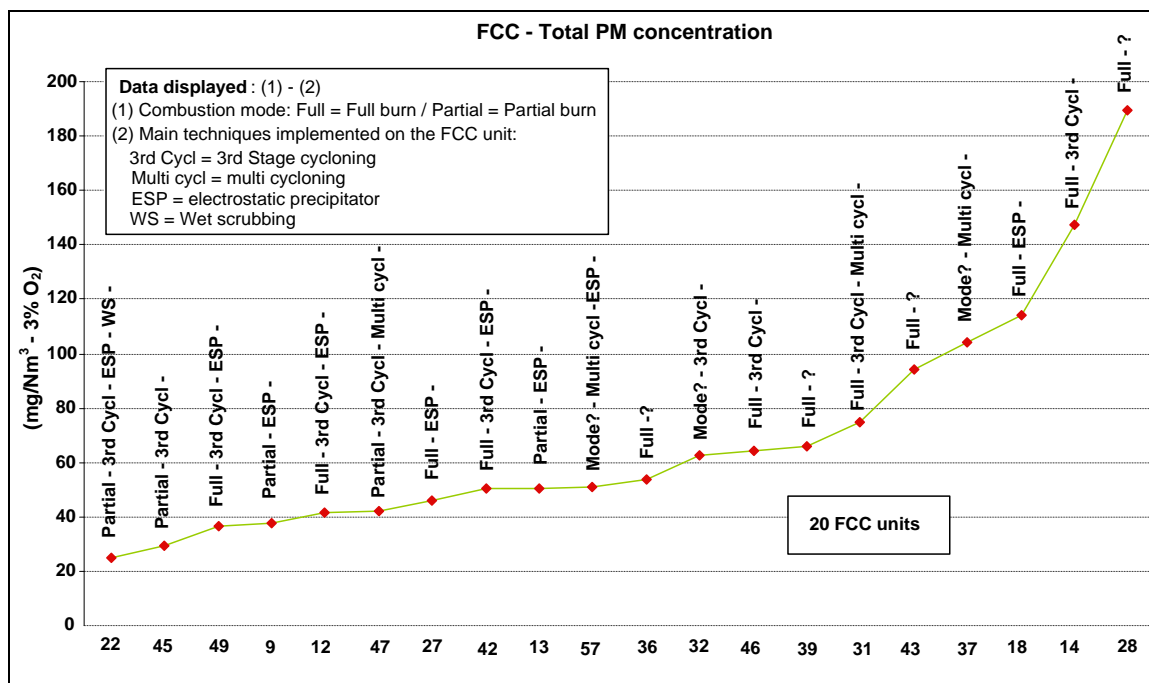


Figure 3.27: PM yearly average concentration from a sample of 20 European FCC units

Additional data received for 2009 for a hydrotreated feed (F1) FCC full combustion unit show a yearly average of $25 \text{ mg}/\text{Nm}^3$ (Source: TWG Austria: Emission declaration for 2009).

Table 3.38: Example of composition of particulate matter generated by catalytic crackers when feedstock is hydrotreated

| Parameter | Actual value | Dimension |
|---------------------|------------------|------------------------------------|
| Total particulate | 23 | mg/Nm^3 |
| Mass flow | 2.0 | kg/h |
| Total metal content | <0.1 | % |
| Nickel | 0.05 0.012 | % Ni/PM mg/Nm^3 |
| Vanadium | 0.02 0.005 | % V/PM mg/Nm^3 |
| Platinum | <0.004 <0.001 | % Pt/PM mg/Nm^3 |

Source: [194, Winter 2000]

Particulates emitted by the catalytic cracker regenerator consist predominantly of catalyst particles with a typical size of $10 \mu\text{m}$ maximum. The particle size distribution shows that, by weight, almost 90 % are smaller than $10 \mu\text{m}$. Much of this dust consists of silica/alumina, nickel and vanadium (as well as other metals) present in the feedstock. The deposited coke (including metals) on the catalyst ranges between approximately 4 % and 5 % w/w. Metal compounds are enriched in the heavy residues during distillation, and are therefore present in the FCC

feedstock. If hydrotreated heavy residues are used as FCC feed, heavy metal concentrations will be smaller.

Sulphur oxides

The sulphur in the feed to the catalytic cracker is split between liquid product streams: H₂S in the gaseous products and SO₂ emissions from the regenerator, with the approximate ratio of 50/45/5. In the case of a RCC, the SO₂ emissions from the regenerator can reach 20 – 30 % of sulphur in the feed. The degree of sulphur dioxide leaving the exhaust gases from the catalytic cracker depends on the sulphur content of the feedstock used, as well as the technology used to control these emissions. SO₃ aerosols will also contribute to the catalytic cracker stack plume opacity.

Figure 3.28 displays SO₂ yearly average concentrations achieved in 2007 – 2008 for a sample of 24 European FCC units. When available, summary information is also given on SO₂-reducing techniques that were implemented at these plants (values are expressed in mg/Nm³ dry at 3 % O₂).

It can be noted that lower emission values are not particularly correlated with the sulphur input in the refinery overall feedstock, nor with the FCC combustion mode. However, best performances are linked to the highest hydrotreatment rates directly applied to the FCC feedstock, and dedicated end-of-pipe treatment techniques that are implemented.

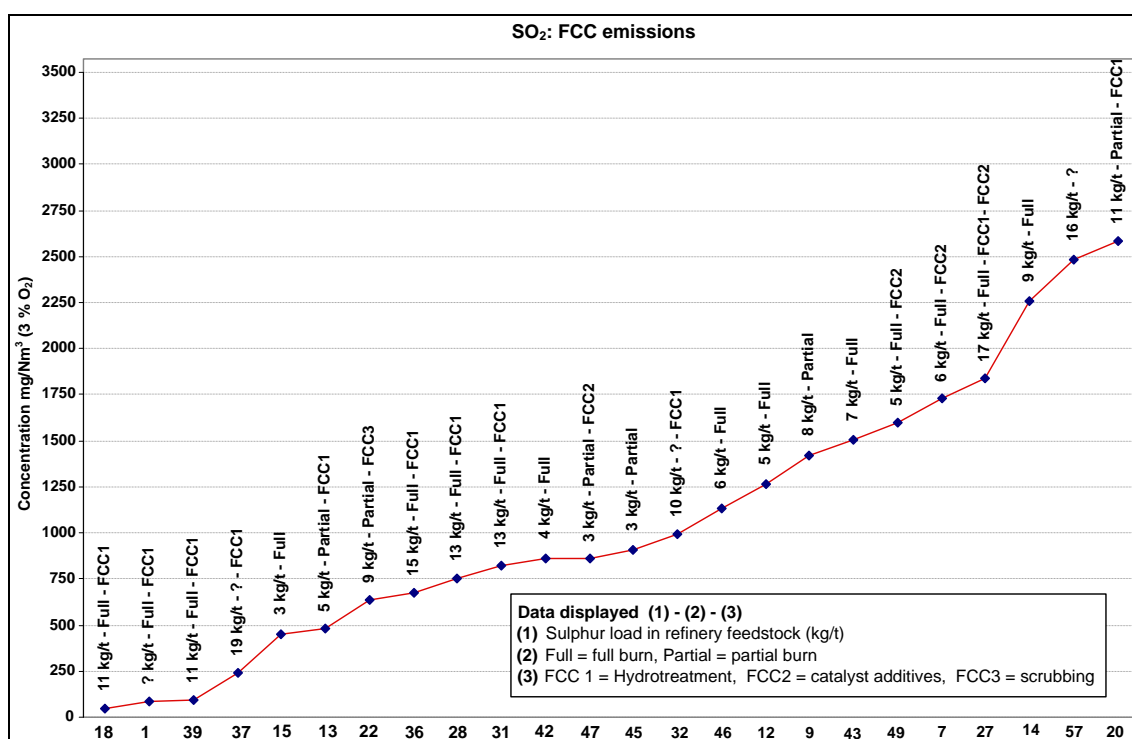


Figure 3.28: SO₂ yearly average concentrations from a sample of European FCC units

Additional data received for a feed hydrotreated (F1) FCC full combustion unit show a yearly average of 82 mg/Nm³ (Source: TWG Austria: Emission declaration for 2009).

Other compounds

Hydrogen sulphide, mercaptans and ammonia may arise from sour waters from reflux condensers. Hydrocarbons (typically 80 % alkanes and typically 15 % olefins) may be released from pressure reliefs, storage and handling operations, spillages and water discharges. Measured dioxin and PAH emission values in two European FCCs are reported below.

Table 3.39: Examples of emission measurements in 2008 of other compounds from two catalytic crackers

| Installation | Abatement techniques | Operational conditions | Total dust mg/Nm ³ | Dioxins ng TEQ/Nm ³ | PAH (16 EPA) µg/Nm ³ | Flue-gas flow/ measurement conditions |
|--------------|--|-----------------------------------|-------------------------------|--------------------------------|---------------------------------|--|
| #1 | ESP, SCR and SO _x -reducing catalyst additive | full combustion without CO boiler | 14 – 23 | 0.002 | 0.46 – 0.6 | 230 000 Nm ³ /h 2.6 – 2.7 % O ₂ |
| #2 | ESP | full combustion without CO boiler | 41 – 46 | 0.002 – 0.03 | 0.41 – 0.73 | 220 000 Nm ³ /h 1.4 – 1.7 % O ₂ |

Average value of three spot measurements under normal operating conditions. *Source:* [77, REF TWG 2010]

3.5.2.2 Waste water emissions

The typical flow of waste water generated by a catalytic cracking process is around 60 – 90 litres of waste water per tonne of feedstock treated. Generated waste water is typically from sour water drains and spillages from the fractionator containing some hydrocarbons: high levels of oil, COD, suspended solids, sulphur compounds (H₂S), phenols, cyanides and ammonia. The next table shows an example of loads and composition of waste water generated in the catalytic crackers.

Table 3.40: Waste water emissions generated by catalytic crackers

| Source of waste water | Parameter | Value | Units |
|--|------------------------------------|------------|-------------------|
| Steam used to purge and regenerate catalysts | Metal impurities from the feed oil | NA | ppm |
| Fractionator overhead reflux drum | Percentage of feed intake | 7 – 10 | % v/v |
| | Flow | 20 – 40 | m ³ /h |
| | H ₂ S | 10 – 200 | ppm |
| | HCN | >1 | ppm |
| | COD | 500 – 2000 | ppm |
| | N-Kj | 15 – 50 | ppm |
| | Phenols | 5 – 30 | ppm |
| Caustic washing of hydrocarbons | Free oil | 50 – 100 | ppm |
| | Flow | 128 | m ³ /h |
| | Phenolic caustic | NA | |
| | Cresylic acids | NA | |

3.5.2.3 Solid wastes

There are potential releases into land from catalyst in the form of fines from particulate matter arrestment equipment and intermittent spent catalyst discharge. These solid residues are enriched in the heavy cycle oil and clarified oil (distillate of FCC unit) fractions. Catalyst addition rates for operation depend on feed metal levels. Addition rates shown are typical values covering a feed metal range of 10 – 20 ppm Ni+V+Na.

Table 3.41: Solid wastes generated in the catalytic cracking

| | Source | Flow | Composition min./max. |
|---|----------------------------------|-------------------------------------|---|
| Replacement of old catalyst during turnaround maintenance | Regenerator | 50 tonnes/4 yr | Spent catalyst: Grey, solid powder consisting of Al ₂ O ₃ , SiO ₂ , carbon, refractory material and metals |
| Catalyst fines | Regenerator overhead cyclone/ESP | | Dust containing high levels of V, Ni, Sb |
| Tank sludge slurry | | Depends on slurry filtration system | 10 – 30 % oil, depending on draining for cleaning, PAH |

3.6 Catalytic reforming

Consumption

Table 3.42 shows a summary of the utilities and catalyst requirements for catalytic reforming.

Table 3.42: Examples of utilities requirements for catalytic reforming

| Utilities | Reforming | Semi-regenerative process | Continuous regeneration process |
|--|---------------|---------------------------|---------------------------------|
| Electricity, kWh | - | 246(*) | 6 142(*) |
| Specific consumption (kWh/t) | 25 – 50 | 55 | - |
| Fuel fired, GJ | - | 185(*) | 232(*) |
| Specific fuel consumption (MJ/t) | 1 400 – 2 900 | 71.5 t/kt | - |
| Cooling water, (m ³ /t, ΔT=10 °C) | 1 – 3 | 0.12 – 3 | 5.5 |
| High-pressure steam generated, kg/t | 50 – 90 | 64 – 90 | 97 |
| Boiler feed water, kg/t | | 170 | 22 |
| Condensate return, t/h | | 88 | 113 |
| Specific value (t/kt) | | 20 | - |
| Catalyst (containing Pt) t/(Mt/yr) | 1.35 | | |

(*) Values related to a capacity of 2 351 t/d. Specific values related to capacity values.
 NB: First column gives ranges for all types of reformers.
 Sources: [168, VROM 1999], [175, Meyers 1997], [204, Canales 2000]

Emissions

Emissions to air

Air emissions from catalytic reforming arise from the process heater gas, fugitive emissions (hydrocarbons from pressure relief valves and leakages) and regeneration. Hydrocarbons and dust releases may arise from venting during catalyst replacement procedures and during clean-out operations.

In the reforming process, very little of the naphtha feed is converted to coke requiring regeneration. In the regeneration process of the catalyst in a continuous catalyst regeneration (CCR) reforming unit, catalyst fines are withdrawn, the coke (0.05 – 0.5 kg coke/tonne feed) is burnt off with hot nitrogen diluted with air. Trace quantities of a promoter (chlorine precursor), normally an organic form of chlorine (such as tri- or per-chloroethylene) are added to retain the catalyst activity. Moisture is removed and the regenerated catalyst is returned to the reformer.

The off-gas from catalyst regeneration varies with the reforming technology employed and the routing of the off-gas. While the off-gas stream from a CCR is continuous, the regeneration emissions from cyclic or semi-regenerative reforming processes are discontinuous. The regeneration vent gas can contain air with diluted oxygen content, steam, CO₂, traces of HCl, Cl₂, CO (<10 mg/Nm³ [167, VDI 2000]), SO₂, hydrocarbons and low levels of dioxins and furans. Depending on the technology and the system design, the regeneration vent gas may be routed over an adsorption bed, through a caustic scrubber, or combined with a basic water wash system. Air emissions of trace components vary significantly depending on the unit configuration.

In addition, catalyst regeneration can be performed in a wet burning loop or in a dry burning loop. Applying the regenerator following the wet burning loop leads to a high water content in the regeneration gas. In addition, this burning gas stays hot in the loop. The dry burning loop process is different as the regeneration gas is quenched and moisture is removed to get a dry gas. These differences of technology lead to different pollutants emissions (like dioxins and furans).

Table 3.43: Data reported on dioxins emissions from catalytic reforming units

| Sources | Abatement techniques | Operational conditions | Concentration ng TEQ/Nm ³ | Specific dioxins emission ng TEQ/tonne |
|---|---|------------------------|---|--|
| US EPA Study | | | | 0.196 ng/t (semi-regenerative) 1 172 ng/t (CCR) |
| Measurements in 4 Belgian refineries | | | <0.1– 0.13 3.3 – 6.7 <0.01 <0.01 | |
| Measurements in 2 Swedish refineries | a. CCR with regeneration gas recycling loop b. Discontinuous with wet scrubber | 99 % abatement | a. NA b. NA | a. Total load: 0.045 g TEQ/yr b. NA |
| NA: these data have not been made available to the TWG. Source: [77, REF TWG 2010] | | | | |

The differences in unit configuration and regeneration vent gas routing have not always been taken into account. In some designs, the regenerator gas can be treated in a water or caustic scrubber to remove dust, chlorine compounds and SO₂ prior to release to the atmosphere. The storage and handling of organic chlorides used during the regeneration may also lead to releases. The organic chloride compounds used for catalyst regeneration are thermally and catalytically converted to HCl or Cl₂ in the regeneration process.

Waste water

In the reforming unit, with a design that generates waste water (water or caustic scrubbers), the amount of waste water generated is around 1 – 3 litres per tonne of feedstock. The waste water contains high-level oils, suspended solids, COD and relatively low levels of H₂S (sulphides), chloride, ammonia and mercaptans. These compounds may also be found in the stabilising tower used to remove light ends from the reactor effluent. Hydrocarbons from spillages and leaks may occur. A study shows that, in the case of released water, the untreated waste water and spent caustics from the reformers can contain a wide range of PCDD/PCDF concentrations of 0.1 pg I-TEQ_{DF}/l to 57.2 ng I-TEQ_{DF}/l. [227, USAEPA 2000].

Solid wastes generated

Most reformers do not generate a continuous solid waste stream. CCR generate a small quantity of catalyst fines that are collected and sent for platinum reclamation. CCR unit catalyst fines are typically less than 1 tonne per year for a 1.7 million tonnes per year reformer. On average, catalyst life is around 10 years. Other potential discontinuous solid wastes might include spent promoted alumina adsorbents used as chloride guards and spent molecular sieve dryer adsorbents. Some solid wastes may also be generated during the equipment maintenance.

3.7 Coking processes

Consumption

Delayed coking

Table 3.44 shows the energy and process materials usage in the delayed coking process. The amount of required make-up water for the coking process depends on the evaporation losses and the bleed to the desalter. Treated effluent can be used for this. The water used for coke cutting during decoking of the drums contains (un)saturated hydrocarbons and coke particles.

Table 3.44: Utility requirements of a delayed coking process

| Fuel (MJ/t) | Electricity (kWh/t) | Steam consumed (kg/t) ⁽¹⁾ | Steam produced (kg/t) | Cooling water (m ³ /t, $\Delta T=17\text{ }^{\circ}\text{C}$) |
|---|---------------------|--------------------------------------|-----------------------|---|
| 800 – 1 200 | 20 – 30 | 50 – 60 | 50 – 125 | 6 – 10 |
| NB: Electricity including the electric motor drives for the hydraulic decoking pump. (¹) Taking into account the ensemble (including the gas concentration integrated unit) will lead to a steam consumption around three times the production. | | | | |

Flexicoking

Table 3.45 shows the energy and process materials usage in flexicoking.

Table 3.45: Utility requirements in the flexicoking process

| Electricity (kWh/t) | Steam consumed (kg/t) | Steam produced (kg/t) | Cooling water (m ³ /t, $\Delta T=10\text{ }^{\circ}\text{C}$) |
|---------------------|-----------------------|-----------------------|---|
| 60 – 140 | 300 – 500 (MP) | 500 – 600 (HP) | 20 – 40 |

Calcliner

The calciner specific energy consumption and production figures are given per tonne of calcined coke produced in Table 3.46.

Table 3.46: Typical utility requirements in the calcinating unit (updated TWG 2010)

| Electricity (kWh/t) | Refinery fuel gas (kg/t) | Steam produced | Steam consumed (kg/t) |
|---------------------|--------------------------|--------------------|-----------------------|
| 13.2 | 0.03 | 2.2 t/h (115 barg) | 2.4 |

Emissions

The most important emissions (and also health and safety aspect of these processes) is the handling of the coke fines.

Emissions to the air

Air emissions from coking operations include the process heater flue-gas emissions and fugitive emissions. In addition, the removal of coke from the drum (delayed coking) can release particulate and any remaining hydrocarbons to the atmosphere. The main pollutants generated, as well as the sources, are described below.

- Hydrogen sulphide and sulphur compounds as mercaptans may be released from the sour water stream from reflux condensers.
- Hydrocarbons may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling operations, spillages and waste and water discharges.

- Particulate matter may be released from the kiln gas cleaning system, the rotary coker gas cleaning system, coke handling and storage, loading operations and from the calcining process. The back pressures of the gas discharges from the kiln are critical to maintain the flame front in the kiln. This could mean the cyclone operating conditions are dictated by the requirement of the kiln rather than the optimum conditions for dust removal. Overall particulate emissions of 10 – 460 mg/Nm³ are achieved [156, MCG 1991], [195, Krause 2000]. Storage, crushing and handling of green coke take place in the wet state with no releases to air. Typical size distribution profiles for particulate matter in calciner exhaust gases after passing through a cyclone system are given in Table 3.47.

Table 3.47: Typical size distribution profiles for PM emitted from calciner cyclone systems

| | |
|----------------|-------------|
| 99 % w/w below | 100 microns |
| 98 % w/w below | 45 microns |
| 90 % w/w below | 8 microns |
| 60 % w/w below | 5 microns |
| 20 % w/w below | 2.5 microns |
| 10 % w/w below | 1.5 microns |

Waste water

Waste water is generated from the coke removal, water bleed from coke handling, sour water from fractionator overhead, cooling operations and from the steam injection and should be treated. The amount of waste water generated in the coking processes is around 140 litres per tonne of feedstock. It contains H₂S, NH₃, suspended solids (coke fines with high metal contents), COD, high pH, particulate matter, hydrocarbons, sulphur compounds, cyanides and phenols. Detailed analysis of the contaminants of such waste waters is not available because they are transferred directly to the refinery main waste water system for treatment.

Solid wastes

Solid wastes generated in the coking processes are coke dust (carbon particles and hydrocarbons) and hot oil blowdown sludges containing hydrocarbons. Table 3.48 shows a typical analysis of these sludges.

Table 3.48: Typical chemical characterisation of the sludge generated in the coker

| Species | Concentration (ppm) | Species | Concentration (ppm) |
|-----------|---------------------|----------------|---------------------|
| Solids | 91.4 % | Selenium | 53 |
| Oil | 8.6 % | Antimony | 40 |
| Carbon | 28.5 % | Nitrate | 35.8 |
| Hydrogen | 3.5 % | Naphthalene | 32.4 |
| Nitrogen | 0.3 % | Vanadium | 32 |
| Iron | 80537 | Phenan | 20.1 |
| Sulphur | 27462 | Phenol | 11.2 |
| Calcium | 8166 | Arsenic | 10.5 |
| Aluminium | 3098 | Toluene | 7.8 |
| Magnesium | 2237 | Fluorine | 6.7 |
| Sulphide | 613.0 | Pyrene | 6 |
| Sodium | 459 | Benzo(A)Pyrene | 5.6 |
| Lead | 272.9 | Benzene | 2.2 |
| Nickel | 230.4 | Ethylbenzene | 2.2 |
| Chromium | 166.7 | Mercury | 1.0 |
| Xylene | 145.4 | Cyanide | 1.0 |
| Sulphate | 115.0 | | |

NB: Figures quoted on a moisture-free basis.
Source: [156, MCG 1991]

3.8 Cooling systems

The information given in this section should be read in conjunction with the ICS BREF, [69, COM 2001] the reference document on industrial cooling systems, particularly the extensive coverage it gives to the consumption of additives.

The need for cooling in a refinery depends on the processes used and on the degree to which they are integrated but, where water cooling systems are applied, it certainly accounts for the majority of water usage. In a refinery, it is important to maximise heat integration at a plant level and at a process/activity level to minimise cooling duty. Therefore, energy requirements for cooling will depend on the cooling system used, together with the cooling strategy applied.

Table 3.49 shows a typical split of the cooling needs in a refinery (hydrocracking refinery with a throughput of 7 Mt/yr).

Table 3.50 gives a distribution of the cooling capacity according to temperature range within a typical refinery (hydrocracking refinery with a throughput of 7 Mt/yr).

Table 3.49: Cooling needs in a refinery

| Application | Cooling capacity | |
|--|------------------|-----|
| | MW | % |
| Process streams | 400 | 94 |
| Pumps, compressors | 10 | 2 |
| Vacuum systems | 15 | 4 |
| Total | 425 | 100 |
| <i>Source: [169, Bloemkolk et al.1996]</i> | | |

Table 3.50: Typical cooling duty according to temperature range

| End temperature (T) process fluid (°C) | Cooling duty | |
|--|--------------|-----|
| | MW | % |
| T>43 | 380 | 95 |
| 43>T>38 | 15 | 4 |
| 38>T>30 | 0 | 0 |
| 30>T | 5 | 1 |
| Total | 400 | 100 |
| <i>Source: [169, Bloemkolk et al.1996]</i> | | |

Consumption

Power is consumed by pumps in a water cooling system and by fans in an air cooling system. The water cooling system uses water and requires chemicals as corrosion and bacterial growth inhibitors. For more detailed information and annual consumption figures, reference is made to the ICS BREF. Both recirculating and once-through cooling water systems require additives, to prevent fouling and/or corrosion. Because once-through systems generally use surface water (either fresh or salted), the chances of fouling are higher, compared to recirculating systems. Therefore, in these systems, more antifouling additives (i.e. chlorinated biocides) should be used. On the other hand, anti-corrosion additives are mainly applied in recirculating systems and not used in once-through systems.

Water utilisation in cooling systems is lower in a recirculating system, compared to a once-through system (up to only 3 %). In the recirculating system, a certain amount of water exits the system through evaporation, as mist droplets and as bleed or blowdown to the waste water treatment system. Therefore, make-up water in the range of about 5 % of the circulation rate is

required, a figure equivalent to the use of 0.23 m³ of cooling water per tonne of crude oil processed. However, to make a balanced comparison between the two kinds of cooling systems, it is necessary to take into account the quality of the water used (often once-through cooling systems are fed with low quality water, marine or brackish water).

Emissions

The main direct environmental impact of the cooling systems is the heat, increasing the temperature of the cooling fluid used. In refinery water cooling, the increase of the temperature (ΔT) is around 10 – 15 °C.

Water consumption (mentioned above), energy consumption (pumps, air-cooler fans) and water pollution are the main environmental issues of cooling systems. Other environment-related effects include noise production (cooling tower, pumps, air-cooler fans: 97 – 105 dB(A) at source) and plume formation (cooling tower).

The main pollutants to be considered in water cooling systems are the antifouling additives, and anti-corrosion additives containing zinc, molybdenum, etc. Special attention should be paid to the use of dispersing additives in closed cooling water systems, particularly when the bleed is routed to an oil-separating water treatment unit, where it can interfere with the oil-water separation process. A once-through system coupled with a low rate of leaks and a high volume of water mean that cooling water discharges contain between 0.1 mg/l and 1 mg/l oil. Hydrocarbon emissions to air from cooling towers (as a result of leakages and stripping) may occur. Emissions to the air were reported to vary between 0.5 and 85 g hydrocarbons per m³ cooling water recirculating over the cooling tower [169, Bloemkolk et al.1996]. Cooling by quenching (only used in delayed cokers within refineries) results in high vapour emissions, significant energy losses, substantial water use and severe water pollution.

Table 3.51: Environmental impact of different cooling systems for a typical refinery

| Emission or effect | Once-through | Once-through (closed-loop) | Cooling tower | Cooling tower (closed-loop) | Air coolers | Air-cooled (closed-loop) |
|--|-------------------------------|-------------------------------|---------------------------------|-----------------------------|-------------|--------------------------|
| Water | | | | | | |
| Thermal heat (MW) | 300 | 300 | Negligible | Negligible | | |
| Hydrocarbons (kg/h) | 2.6 – 26 | | | | | |
| Chemical conditioning ⁽¹⁾ (kg/h) | 2.6 | 2.6 | 3 – 25 | 3 – 25 | | |
| Water blowdown discharge (m ³ /h) | 26 000 | 26 000 | 156 | 156 | | |
| Air | | | | | | |
| Visible plume | | | +(³) | +(³) | | |
| Water vapour (kg/h) | | | 468 000 | 468 000 | | |
| Hydrocarbons (kg/h) | | | 13 | (+)(³) | | |
| Energy consumption ⁽⁴⁾ (kW) | 3 500 | 5 500 | 5 600 | 7 000 | 2 000 | 8 700 |
| Fresh water consumption (m ³ /h) | | In closed circuit | 624 | 624 | | |
| Other nuisances | | | | | | |
| Noise ⁽²⁾ | + | + | + | + | + | + |
| Other | Entrainment of fish in intake | Entrainment of fish in intake | Legionella risk in air releases | | | |
| ⁽¹⁾ Hypochlorite in once-through cooling water; anti-corrosives, hypochlorite and anti-scalants in cooling tower make-up water. ⁽²⁾ See text. ⁽³⁾ Suppression of plume possible at extra cost. ⁽⁴⁾ Process energy losses not included. ⁽⁵⁾ Possible effect: the leaking of air coolers is not a well-described phenomenon. The absence of water would suggest that corrosion is not an important factor compared to water-cooled systems. Further study would be needed for an accurate assessment. + Effect occurs. | | | | | | |
| Source: [169, Bloemkolk et al.1996] Completed by TWG 2010 | | | | | | |

3.9 Desalting

The quantity of inorganic impurities in the crude oil depends very much on both the crude origin and the crude handling during transport from the crude well to the refinery.

Consumption

The water used in crude desalting is often untreated or partially treated water from other refining process water sources. Table 3.52 shows the typical operating conditions and water consumption in the desalters, depending on the type of crude oil used.

Table 3.52: Typical operating conditions of the desalting process

| Crude oil density (kg/m ³ at 15 °C) | Water wash (% v/v) | Temp (°C) |
|---|-----------------------|--------------|
| <825 | 3 – 4 | 115 – 125 |
| 825 – 875 | 4 – 7 | 125 – 140 |
| >875 | 7 – 10 | 140 – 150 |

For desalting long or atmospheric residue, 10 % w/w water on feed is common. Once the water and the oily phase have been well mixed, the water should be separated from the oil feedstock in a separating vessel. This is done by adding demulsifier chemicals (5 – 10 ppm) to assist in breaking the emulsion and, in addition, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The electricity consumption used in the desalting processes varies typically from 0.075 kWh to 0.15 kWh per tonne of crude oil.

Emissions

Air emissions

No major emissions to air are produced during the desalting processes. Air emissions from the heating process are expected, and fugitive emissions (hydrocarbons) may be expected.

Solid wastes generated

The quantities of desalter sludge generated depend on the solid content of the crude, the separation efficiency and the applied desludging mode and frequency. Normally a desalter clean-out is done twice a year, yielding from 60 to 1 500 t/yr oily sludge, dependent on the throughput and efficiency of the process to capture solids. The sludge generated can contain iron rust, clay, sand, water (5 – 10 % w/w), emulsified oil and wax (20 – 50 % w/w) and metals.

Waste water

The desalter contributes greatly to process waste water (30 – 100 litres/tonne feedstock desalted). The desalting process creates an oily desalter sludge and a high-temperature salt waste water stream (possibly the most polluted in the refinery), which is typically added to refinery waste water treatment facilities. The waste water generates a wide variety of pollutants and in considerable amounts that can never be discharged without proper treatment. Table 3.53 shows the ranges to be expected from waste waters from desalters.

Table 3.53: Composition of the waste water generated in the desalting process

| Water pollutants | Typical concentration (mg/l) |
|---|------------------------------|
| Temperature (°C) | 115 – 150 |
| Suspended solids | 50 – 100 |
| Oil/oil emulsions | High |
| Dissolved hydrocarbons | 50 – 300 |
| Phenols | 5 – 30 |
| Benzene | 30 – 100 |
| BOD | High |
| COD | 500 – 2000 |
| Ammonia | 50 – 100 |
| Nitrogen compounds (N-Kj) | 15 – 20 |
| Sulphides (as H ₂ S) | 10 |
| <i>Source:</i> [183, HP 1998], [159, WB 1998] | |

3.10 Energy system

The energy system is an important, if not the most important, activity from the environmental perspective. The energy (heat and power) necessary to transform the raw materials to products is provided by the combustion of hydrocarbon fractions that mainly generates emissions to air. As mentioned in Section 2.10, this section contains data on the emissions generated by the energy system as a whole. As a consequence of this, the emissions generated by furnaces or boilers of specific processes are integrated here and they are not considered in the other sections.

3.10.1 Energy management

Energy efficiency in refineries

There are currently three methodologies in use in refineries and these are briefly described below.

- The first is *specific energy consumption (SEC)*. This is the most simple index. It is calculated as the ratio between the energy consumed by the refinery and the tonnes of feedstock processed. According to data gathered by the TWG from a sample of 50 European refineries, the specific energy consumption of European refineries (from 5th to 95th percentiles) ranges from 1.6 to 3.7 GJ per tonne of throughput (crude and intermediates). Because it is a simple index, this ratio does not take account of the complexity of the refinery (more complex refineries tend to consume more energy).
- The second methodology is the *products method*. [230, G. J. M. Phylipsen, K. Blok, et al.1998] This method considers the products and internal energy products produced in the refinery, giving a specific energy consumption benchmark per tonne of energy product produced. Multiplying these specific energy consumption levels by the amount produced within the refinery and adding all the totals together gives an energy consumption benchmark for that refinery. Some calculations based on 2008 data indicate that the best specific energy consumption figures are between 2.4 and 2.9 GJ/tonnes, whereas actual values were from 1 to 4.8 GJ/tonnes. That means that some European refineries are doing better than figures that are considered a good benchmark.
- The third methodology is the *Energy Intensity Index (EII)*. It is a measure used to compare energy consumption in refineries. The standard energy use is based on the energy consumption at more than 500 refineries worldwide. Since the beginning of this benchmarking (property of Solomon Associates) in the 1980s, an EII of 100 corresponds, by design, to the current average calculated for all the participating US plants. The average EII obtained in a worldwide market survey (Solomon study, 1994) was 92, with a range from 62 to 165 [160, Janson 1999]. More energy-efficient refineries correspond to the lower values of EII. Therefore, some refineries are almost three times as energy-efficient as others. In 2005, the top 10 % of all best EII values reported worldwide were equal to or below 75. This index reflects the types of processes and throughput of each process in the refinery. These data are not available for all refineries and typically are considered confidential by refineries. As shown in Figure 3.29, a total of 41 European refineries have reported their EII (2006, 2007 or 2008) in TWG questionnaires, and the values have been plotted together with specific energy consumption calculated for each of the sites concerned. A clear correlation is naturally observed. Within this European sample, EII ranges from 65 to 124, with an average of 93 very close to the world average, and five plants in the best 10 % in terms of worldwide performance.

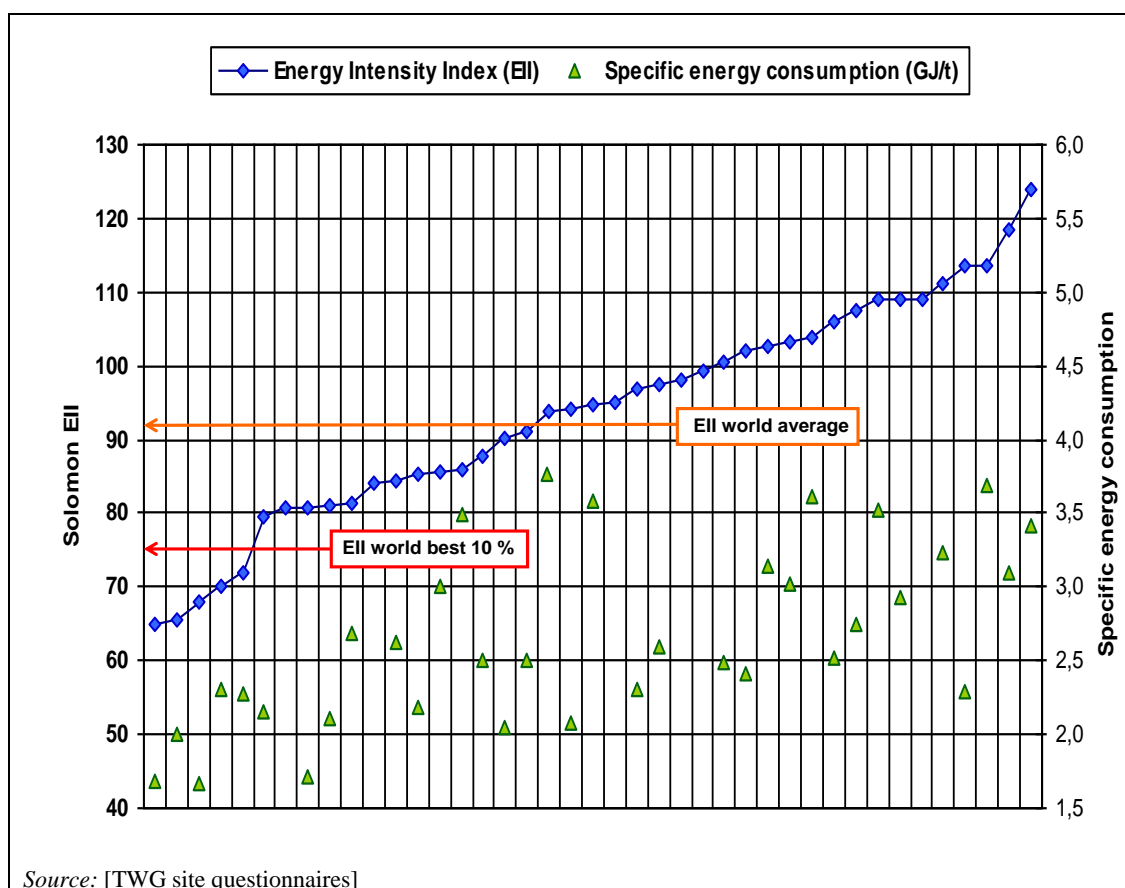


Figure 3.29: Energy Intensity Index and specific energy consumption for 41 EU refineries

3.10.2 Energy capacity and consumption

Capacity of the refinery energy system

The capacity of the individual combustion plants in a refinery varies widely from less than 10 to 200 Megawatts thermal input (MW); and the total installed capacity ranges from several hundred to more than 1 500 MW in the largest refineries. The energy consumed at the combustion plants of the refineries ranges from 200 TJ to more than 17 000 TJ per year. Deep conversion refineries in general use more than three times as much energy (10 % of crude intake) as simple hydroskimming refineries (3 %) [159, WB 1998].

Gasification plant

An IGCC unit produces 130 t/h of syngas mainly composed of CO and H₂ in the ratio 1:1 (calorific values of 9 600 – 10 000 kcal/kg) starting from 58 t/h of feedstock (calorific value of the heavy residue varies between 8 800 and 9 200 kcal/kg, sulphur content: 3.5 – 7 % and metal content: 300 – 800 ppm). A solid effluent in the form of a filter cake (about 160 – 400 kg/h dry) is discharged and sent to external plants for recovery of the metals. Two Claus units recover 4 t/h of elemental sulphur from the H₂S recovered in the acid gas removal section. A tail gas treatment section that permits an overall sulphur recovery of 99.9 %, follows the Claus units [221, Italy 2000].

Refinery fuels

The baseline ratio of gas to liquid refinery fuel used in a refinery is a function of a number of factors, important amongst which are the size, degree of complexity, LPG recovery efficiency and extent to which refinery fuel gas is processed into other products (e.g. olefins) or exported to adjacent chemicals plants (either directly or as energy from common facilities). It varies from 80/20 or 70/30 (gas/liquid) at a stand-alone, moderately complex refinery to 40/60 at a highly complex site which also services a chemicals complex. However, these ratios can be increased when energy conservation measures are applied and the gas availability becomes sufficient for

the energy supply of the refinery. Table 3.54 illustrates the calorific value and the sulphur content of the different fuels.

Table 3.54: Properties of the fuels used within a refinery

| Type of fuel | Calorific value (MJ/kg) | Sulphur content |
|-----------------------------------|-------------------------|--|
| Refinery fuel gas (RFG) | 29 – 49 | 20 – 4 000 mg H ₂ S/Nm ³ |
| Hydrogen gas | 55 – 70 (LHV) | 20 – 1 200 mg H ₂ S/Nm ³ |
| Catalyst coke from FCC | 38 – 40 | 0.11 – 0.3 % S |
| Liquid refinery fuel | 40 | <0.1 – 4 % S |
| <i>Source: [updated TWG 2010]</i> | | |

There are differences in the characteristics of the liquid refinery fuel used in European refineries. The data from a CONCAWE report show that in 2006 about 50 % of oil fired had a sulphur content of ~1 % or less, only 10 % of refineries used oil with more than 2 % sulphur in 2006, compared with 20 % in 2002 and 35 % in 1998. The average sulphur content was 1.7 % in 1998, 1.34 % in 2002 and 1.33 % in 2006 [63, CONCAWE 2010].

Table 3.55 shows the chemical characteristics of three different liquid fuels.

Table 3.55: Chemical properties of several typical heavy liquid oils

| Property | High sulphur | Intermediate sulphur | Low sulphur |
|-----------------------------------|--------------|----------------------|-------------|
| Sulphur % w/w | 2.2 | 0.96 | 0.50 |
| Carbon % w/w | 86.25 | 87.11 | 87.94 |
| Hydrogen % w/w | 11.03 | 10.23 | 11.85 |
| Nitrogen % w/w | 0.41 | 0.26 | 0.16 |
| Ash % w/w | 0.08 | 0.04 | 0.02 |
| Vanadium (ppm) | 350 | 155 | 70 |
| Nickel (ppm) | 41 | 20 | 10 |
| Sodium (ppm) | 25 | 10 | <5 |
| Iron (ppm) | 13 | 9 | <5 |
| <i>Source: [243, Blas 2000]</i> | | | |

The nitrogen and sulphur contents are two of the most important chemical parameters and are responsible among other factors for the emissions of NO_x and SO_x. Ash content combined with high sulphur can directly affect particulate matter emissions. Figure 3.30 shows the distribution of nitrogen and sulphur contents in various types of vacuum residues according to their geographical origin.

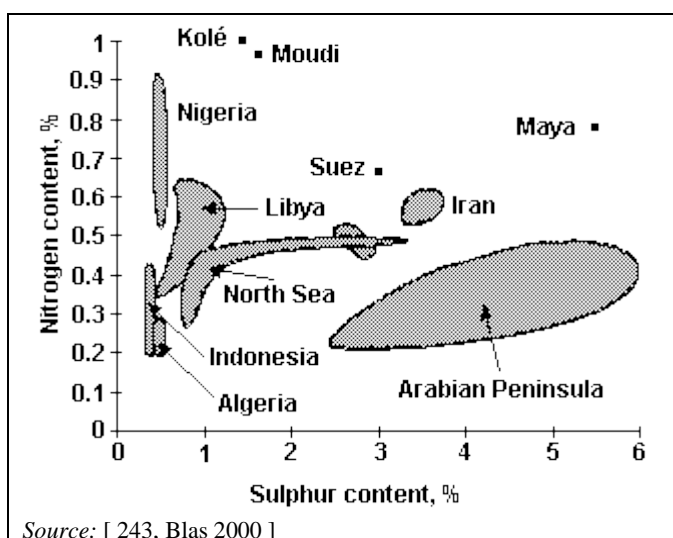


Figure 3.30: Sulphur and nitrogen contents in HFO (vacuum residues) according to their geographical origin

Steam generation

Steam generation requires an energy input of 2 700 – 3 200 MJ per tonne of steam produced. Conditioning chemicals are dosed to the BFW in low concentrations and comprise the following groups of chemicals: anti-scaling agents, corrosion inhibitors and anti-foaming agents. A 100 t/h steam generation system requires approximately 1.5 – 3 t/yr corrosion inhibitors and 2 – 4 t/yr anti-scaling agents. These conditioning chemicals included are:

- Corrosion inhibitors (mainly oxygen scavengers and alkaline compounds). Sulphite (<60 bar), oximes, hydroxyl amines, and hydrazine (declining use due to safety issues) etc. are commonly applied as oxygen scavengers for deaerated boiler feed water prior to pumping into the boiler. Commonly applied alkaline compounds are sodium phosphates (which are also hardness binders), caustic, ammonia and neutralising amines.
- Anti-scaling agents such as polyacrylates and phosphonates that are rest hardness binders and dispersing agents.
- Anti-foaming agents, in general intermittently dosed, to combat foaming in case the condensate contains oil or organics.

3.10.3 Emissions

3.10.3.1 Air emissions

General aspects

Since emissions to water are minimal and very little is generated in the way of solid waste, emissions to air are the primary emissions, both from the energy system and from the refinery as a whole. The sum of flue-gas flows generated from all combustion processes associated with the energy system (i.e. central power plant, process furnaces, stand-alone boilers and eventual gas turbines) in a refinery range from around 1 to 20 GNm³/yr (0.1 to more than 2 million Nm³/h at 3 % O₂), which corresponds to 0.2 – 2 million Nm³/t of feedstock processed.

The main releases to air from combustion processes are stack gases containing oxides of sulphur, oxides of nitrogen, oxides of carbon (carbon monoxide and carbon dioxide) and – particularly important when liquid refinery fuel or coke is combusted – particulate matter, including PM₁₀ and metals (e.g. V, Ni). When operating properly and when burning cleaner fuels such as refinery fuel gas, low-sulphur fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significantly higher. Incomplete combustion may lead to releases of

carbon monoxide, smoke and, if heavy fuel oils are used, particulate matter. As a result, combustion plants are major contributors to the release of air emissions from refineries. The level of pollutants emitted will depend on the quality of the fuels burnt, which can vary considerably. There are conflicting factors in a combustion process which contribute to emission levels. For example, combustion conditions which favour low particulate emissions for liquid refinery fuel, i.e. excess air, high temperature, good air/fuel mixing and good fuel-atomisation, are not favourable for low NO_x emissions.

Refinery fuel gas, if properly treated, is a low polluting fuel. Liquid refinery fuels generate more emissions to the air than refinery fuel gas. Gas-fired heaters and boilers generate little dust and lower SO₂ emissions, as the refinery fuel gases are usually cleaned in amine scrubbers. NO_x emissions are also much lower than those of liquid-fired boilers and heaters.

By way of example, Table 3.56, Table 3.57 and Table 3.58 show, respectively, the air emissions generated by gas and liquid refinery fuels in two power plants in European refineries.

Table 3.56: Air emissions from boilers and furnaces fired with refinery fuel gas

| Fuel Consumption (GWh/yr) | Throughput (t/yr) | Units | CO ₂ | CO | NO _x | Particulates | SO ₂ |
|--|-------------------|-------------------|-----------------|------|-----------------|--------------|-----------------|
| 561.4 | 41 000 | mg/m ³ | | <80 | <100 | 1 | 1 – 20 |
| | | t/yr | 108 917 | 23.6 | 75.7 | 0.6 | 74 |
| | | kg/t feed | 2 657 | 0.58 | 1.85 | 0.014 | 1.81 |
| NB: Data in table refer to daily average, 3 % O ₂ , dry. Source: [191, UBA Austria 1998] updated TWG AT 2010 | | | | | | | |

Table 3.57: Air emissions from a power plant fired with heavy fuel oil

| Fuel consumption (GWh/yr) | Through put (t/yr) | Units | CO ₂ | CO | NO _x | Particulates | SO ₂ |
|--|--------------------|-------------------|-----------------|---------|-----------------|--------------|-------------------------|
| 4 821.5 | NA | mg/m ³ | - | 18 – 79 | 60 – 98 | 2 – 3 | 55 – 159 ⁽¹⁾ |
| NB: Data in table refer to monthly average, 3 % O ₂ , dry. Vacuum cracked flashed residue from the thermal gas oil unit is co-fired. (¹) The flue-gas is treated in a SNO _x plant. RFG and natural gas are co-fired with heavy fuel oil. Source: [191, UBA Austria 1998] updated TWG AT 2010 | | | | | | | |

Figure 3.31 and Figure 3.32 show the 2009 emissions data for SO₂, NO_x and dust from large combustion plants in refineries reported by the Member States to the Commission.

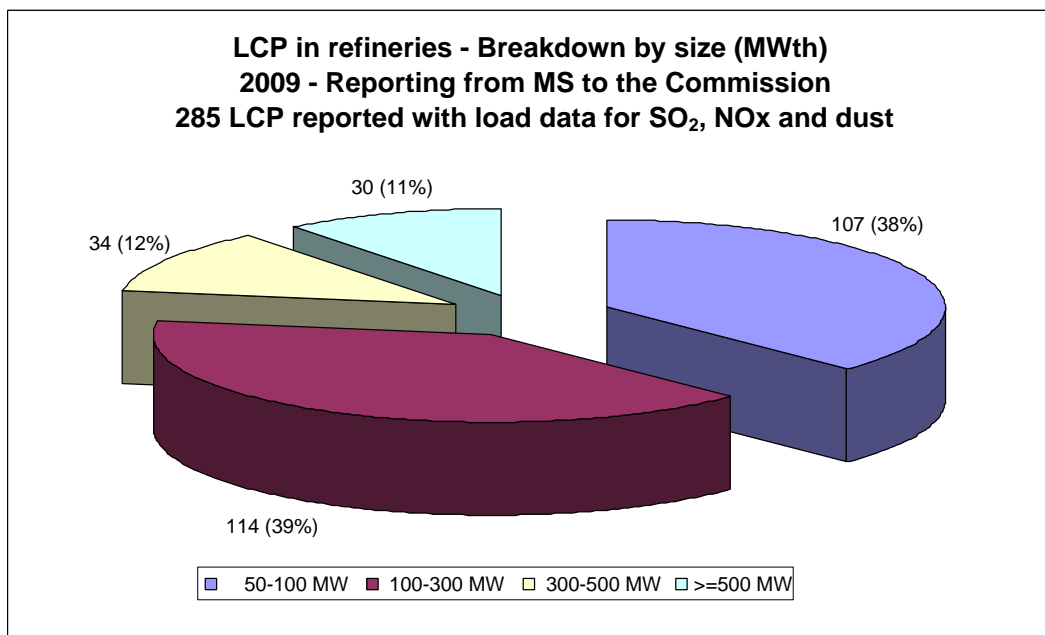


Figure 3.31: Large combustion plants in refineries' 2009 reporting of Member States to the Commission

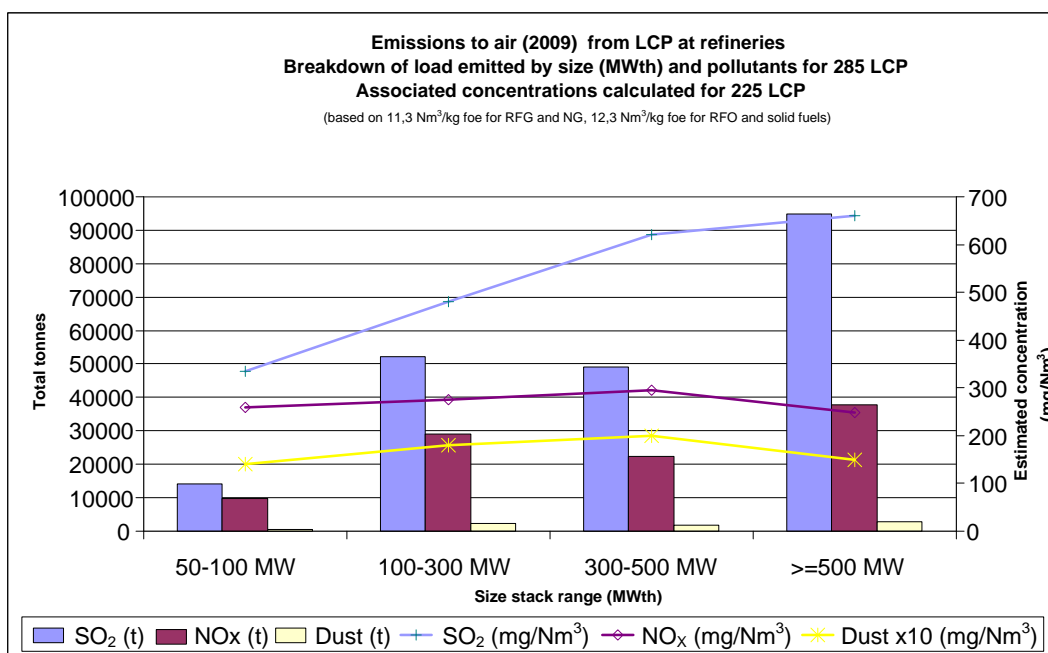


Figure 3.32 Emissions to air from LCP in refineries: loads and associated concentrations

Table 3.58: Air emissions from TOTAL Mitteldeutschland refinery power plant burning refinery liquid residue

| Emissions parameters | Raw gas | Clean gas |
|--|-----------|-----------|
| Volume, wet (m ³ /h, 7 % O ₂) | 171 690 | 188 249 |
| Gas temperature (°C) | 180 – 200 | up to 72 |
| Particulates (mg/m ³ , 3 % O ₂) | 220 | <10 |
| NO ₂ (mg/m ³ , 3 % O ₂) | 800 | <150 |
| SO ₂ (mg/m ³ , 3 % O ₂) | 6 500 | |
| SO ₃ (mg/m ³ , 3 % O ₂) | 650 | <10 |
| SO _x as SO ₂ (mg/m ³ , 3 % O ₂) | | <400 |
| NB: It includes a FGD process. Liquid refinery fuel contains 7 % sulphur. Source: [191, UBA Austria 1998] | | |

Carbon dioxide

Combustion processes of fossil fuels produce CO₂ as a result of the combustion of hydrocarbons. The amount of CO₂ emitted to the atmosphere by European refineries varies from 0.15 to 5.5 million tonnes per year (range depending on the type of refinery and the energy integration). The specific CO₂ emissions (calculated from 5th to 95th percentiles within a sample of 58 European refineries) range from 0.1 to 0.4 tonnes of CO₂ per tonne of feedstock processed. CO₂ emissions from power plants in the refineries correspond to around 42 % of the CO₂ emitted by the refinery. The use of liquid fuels results in lower thermal efficiencies and higher CO₂ emissions than the use of gaseous fuels.

Table 3.59 shows the sources (type of fuels) of the CO₂ emissions of the refining industry. The table also includes the calculated emission factors for CO₂ for various refinery fuels.

Table 3.59: CO₂ emission factors for different types of fuels

| Fuel type | Typical composition (% w/w) | kg CO ₂ /kg fuel | kg CO ₂ /GJ |
|---|---|-----------------------------|------------------------|
| Refinery fuel gas (RFG) | 30 H ₂ /35 C ₁ /35 C ₂ % v/v | 2.83 | 43 |
| Natural gas (NG) | 100 % methane | 2.75 | 56 |
| Liquefied Petroleum Gas (LPG) | 50 C ₃ /50 C ₄ | 3.02 | 64 |
| Distillate Fuel oil | 60 P/10 O/30 A | 3.22 | 74 |
| Residual Fuel | 50 P/50 A | 3.26 | 79 |
| Coke | 90 C/10 ash | 3.30 | 117 |
| NB: abbreviations: Carbon, Hydrogen, Paraffins, Olefins, Aromatics Sources: [166, CONCAWE 1999], [202, Dekkers 2000] | | | |

Carbon monoxide

One of the products of partial combustion processes is carbon monoxide. The CO emissions, which range from 20 to 42 mg/Nm³ at 3 % O₂, are very dependent on the type of fuel used and the completeness of the combustion process. Specific emission values for CO are 0.58 kg CO per tonne of refinery fuel gas and 0.24 kg CO per tonne of liquid fuel.

Nitrogen oxides

NO_x emissions from a refinery energy system depend on the fuel type, fuel nitrogen or hydrogen content, combustor equipment design and operating conditions. The formation and release of NO_x from combustion processes arises from the oxidation of nitrogen present in the fuel source and/or the air used. Accordingly, large differences in the NO_x emission level can be expected between refineries and even between different combustion installations at the same refinery at different times. Differences in temperature, residence time and oxygen concentration

result in varying levels of thermally formed NO_x. The influence of temperature is most important, with NO_x emissions increasing exponentially with temperature.

Gaseous fuels typically release less NO_x per unit of energy compared with liquid fuels, especially liquid refinery fuels. Oil burning normally leads to higher levels of NO_x releases for several reasons: the problem of fuel NO_x arising from the nitrogen content (0.03 – 1 %), the way in which the plant is often operated so as to balance NO_x and particulate releases, and the frequent design requirement for firing in combination with gas. However, the latter statement is only true for non-abated emissions, since the inclusion of secondary measures can reduce both NO_x and particulate emissions. One refinery in 1996 found that fuel oil can generate about three times more NO_x than gas fuels. NO_x factors (NO_x produced per tonne of fuel combusted), used by some refineries to report NO_x emissions, indicate NO_x from oil firing to be two to three times that from gas firing.

Figure 3.33 gathers the NO_x equivalent concentrations (expressed as yearly averages in mg/Nm³ dry at 3 % O₂) of all flue-gases emitted by the overall energy system of some European refineries. For each site, summary information is given on the existence of typical NO_x-related techniques implemented at various parts of the energy system, and on the portion of total gaseous fuels (refinery fuel gas + eventual external natural gas supply) in the site energy mix. Most sites emit in the range of 100 – 500 mg/Nm³. As expected, a clear correlation is observed between the highest gaseous fuel ratios in the site energy breakdown and the lowest NO_x equivalent concentrations.

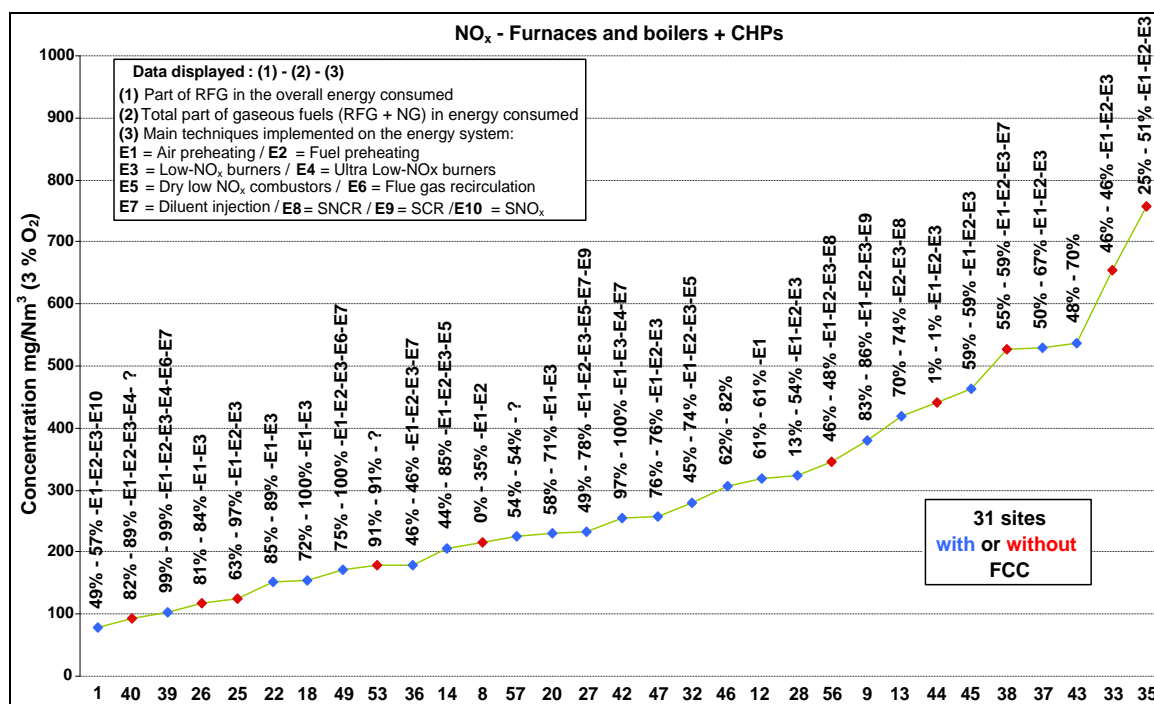


Figure 3.33: Distribution of NO_x yearly average equivalent concentrations from the energy system of a sample of European refineries

Additional data received for 2009 show, for the energy system, a yearly average of 71 mg/Nm³ of NO_x emissions (*Source*: Questionnaire 1 updated with emission declaration for 2009).

The fired heaters, boilers and gas turbines running on refinery blend gas generate lower NO_x emissions than FCCs. Specific NO_x emissions related to energy consumption range from 15 to 200 mg/MJ for furnaces with 100 % gas fuel. Specific NO_x emissions related to the throughput range from 84 to 700 tonnes of NO_x per million tonnes of crude oil processed. The NO_x load ranges from 20 to more than 2 000 tonnes per year.

Particulates

Under normal operating conditions, the solids in the flue-gases of a furnace or boiler consist mainly of coke particles with some cenospheres, depending on firing conditions. The particulate emissions of oil-fired equipment may vary considerably since they depend on a number of more or less independent parameters such as: fuel type, burner design, oxygen concentration at the outlet of the radiant section, the flue-gas outlet temperature of the radiant box, and the residence time of the fuel droplets. The particle size of the particulate matter (PM) from furnaces and boilers on HFO is in the order of 1 μm . The PM in flue-gases can take any of the following four forms:

- soot where the particle size is below 1 μm (the visible smoke from a stack is caused by all particles but mainly those with a particle size between 0.5 and 5 μm);
- cenospheres: they originate from the liquid phase wastes of combustion of heavy oil droplets at relatively low temperature (<700 °C), the size is equal to or larger than that of the original oil droplets;
- coke particles, formed through liquid phase cracking in combustion at high temperatures (>700 °C), the particle size is generally from 1 to 10 μm ;
- fine particles (<0.01 μm): their contribution to the total mass emission is negligible.

The PM in the flue-gas of furnaces and boilers fired with heavy fuel oil is a mix of metal compounds and soot/coke. Metals (mainly V and Ni) are a natural constituent (indigenous) of the crude. Soot and coke result from imperfections of the combustion process. Contaminants such as sand, rust and other metals, and coke particles of the fuel itself, may also contribute to the formation of particulates. The indigenous metal content of the heavy fuel oils (see Section 2.10), which can be calculated from the metal content of the crude oil from which the HFO is made, is the basis for calculating the minimum ash content of the HFO and therefore also the basis for the PM in the flue-gas. Ash contents are higher than the metal content itself (as the metal compounds are in the ash), and generally lie in the range of 500 – 1 500 ppm (0.05 – 0.15 % w/w). In practice, the PM content is normally higher by a factor of 2 – 4, because unburnt fuel (soot) adheres to the metallic PM, and because aerosols of SO_3 are also monitored as PM.

The range of the unabated PM (150 – 500 mg/Nm^3) is typical for the current burners application (steam atomisation and low- NO_x), assuming all measures are taken to achieve good combustion (optimum oxygen content and lowest practicable NO_x in the flue-gas), and is directly related to the ash content of the fuel. For older furnaces, liquid refinery fuel-fired flue-gas levels may range from 500 to 1 000 mg/Nm^3 . For boilers, the figures are on average lower. For a new optimal burner design with steam atomisation this can be well below 200 mg/Nm^3 . The range of 150 – 500 mg/Nm^3 represents the current typical range with liquid refinery fuels employed (ash contents) and burners installed (low- NO_x with steam atomisation). Table 3.60 shows the particulate emission range found in current European refineries.

Table 3.60: Particulate emissions ranges for existing installations

| | Refinery fuel gas | Liquid refinery fuel |
|---|-------------------|----------------------|
| Process furnaces | 0.4 – 2.4 | 5 – 1 000 |
| Boilers | <5 | 5 – 500 |
| CHP | - | 2 – 3 ⁽¹⁾ |
| NB: All figures in mg/Nm^3 at 3 % O_2 (monthly average). | | |
| ⁽¹⁾ The flue-gas is treated in a SNO_x plant. RFG and natural gas are co-fired with heavy fuel oil. | | |
| Sources: [151, Sema, Sofres 1991], [191, UBA Austria 1998] updated TWG NL 2010 | | |

Soot blowing is an operation that is carried out at regular intervals to remove soot from the furnace that is accumulating on the furnace equipment and hampers proper functioning. During

this operation the PM content of the exhaust gas can reach values of 2 000 mg/Nm³. Abatement techniques installed for normal operating conditions will be effective to reduce the PM emissions from this operation.

Sulphur oxides

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Heavy fuel oil residues normally contain significant proportions of sulphur and nitrogen, depending mainly on their source and the crude origin. Data from the 2006 CONCAWE sulphur survey [63, CONCAWE 2010] show that the average SO₂ content in the flue-gas of refinery energy systems (from oil/gas firing) has been roughly reduced by a factor of almost two between 1998 and 2006. The weighted average concentration has been calculated to be 594 mg/Nm³.

Figure 3.34 gathers the SO₂ equivalent concentrations (expressed as yearly averages in mg/Nm³ dry at 3 % O₂) of all flue-gases emitted by the overall energy system of some European refineries. For each site, a summary of information is given on factors likely to influence SO₂ emissions from the refinery combustion plants concerned: the sulphur input from the overall feedstock, and the portion of total gaseous fuels (refinery fuel gas + eventual external natural gas supply) in the site energy mix. Most sites emit in the range of 50 – 1 500 mg/Nm³. As expected, a clear correlation is observed between the highest gaseous fuel ratios in the site energy breakdown and the lowest SO₂ equivalent concentrations reported here.

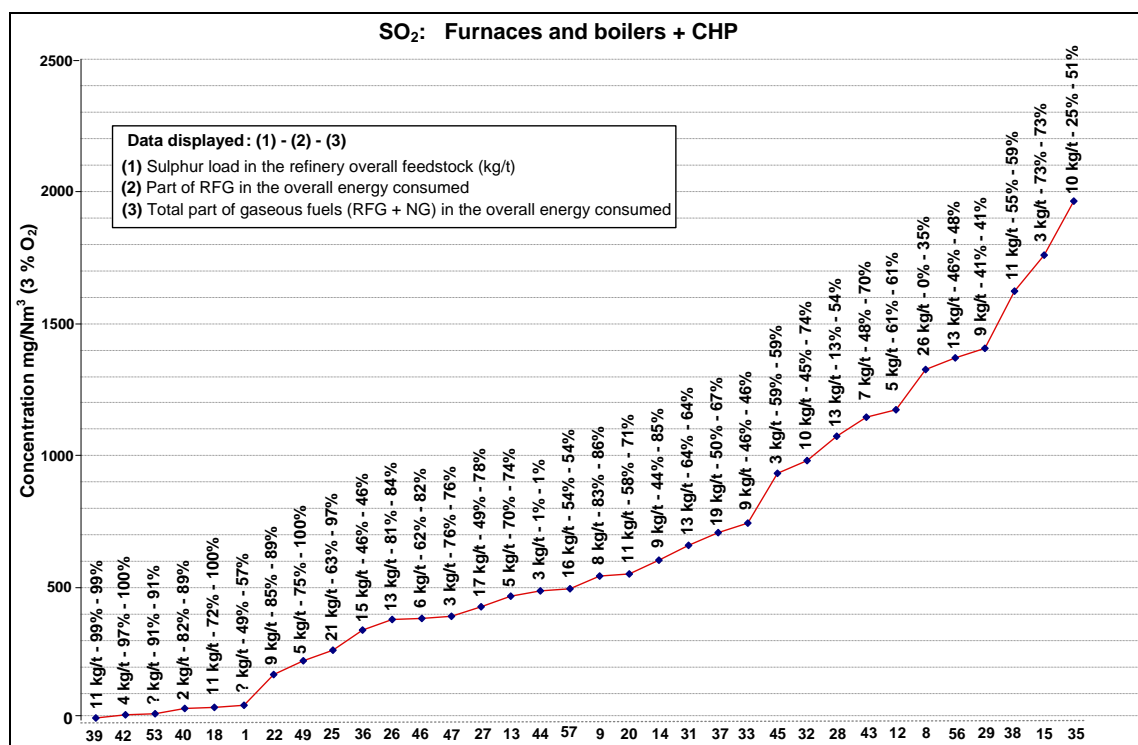


Figure 3.34: Distribution of SO₂ yearly average equivalent concentrations from the energy system of a sample of European refineries

In air-blown gasification of coke, the sulphur content will be about 4 000 mg/Nm³ per unit of % sulphur in the feed.

3.10.3.2 Waste water

Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. The waste water generated in the energy processes comes mainly

from the boiler feed water (BFW) system (i.e. demineralised water plant and condensate treatment plant). The main streams are the boiler blowdown (1 – 2 % of the BFW intake) and the BFW preparation regeneration wash (2 – 6 % of the BFW produced). The main pollutants and composition of the first stream are COD: 100 mg/l; N-Kj: 0 – 30 mg/l; and PO₄: 0 – 10 mg/l. The BFW preparation regeneration stream is combined with NaOH/HCl for pH neutralisation. Normally no biotreatment is required.

3.10.3.3 Solid wastes generated

Releases to land may result from the routine collection of grit and dust and arisings during cleaning procedures. The composition is 0.5 – 1 % w/w Ni and 2 – 3 % w/w V in furnaces and 1 – 3 % Ni/V for boilers. The amount depends on the furnace design and the liquid fuel quality, but in boilers varies from zero to 10 tonnes per year. Liquid refinery fuel tank bottom sludge may be generated in the storage tanks. Sludge may also be generated from the cleaning of fouled exchanger bundles. The flow depends on the liquid refinery fuel quality and the presence of fuel tank mixers. Depending on the mode of draining, 20 – 80 % is oil.

3.11 Etherification

Consumption

The etherification reaction is exothermic, and so cooling to the proper reaction temperature is critical in obtaining optimal conversion efficiency. Methanol is needed for the production of these ethers. The utility consumption levels in Table 3.61 are specified per tonne of MTBE processed in an oxygenate unit.

Table 3.61: Utility requirements in the etherification processes

| Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, $\Delta T=10^{\circ}\text{C}$) |
|------------------------|--------------------------|--|
| 12 – 20 | 1 000 – 2 000 | 2 – 8 |

Emissions

Air emissions

Potential releases of hydrocarbons into air come from pressure reliefs on vessels, depentaniser column overheads drum and distillation column reflux drum, methanol plant, steaming vents on scavengers and reactor catalyst.

Waste water

Potential releases of hydrocarbons, methanol and ethers to water come from spillages and water bleed from methanol recovery. The water bleed is generated at a flow of 1 – 2 m³/t and with a composition of COD of 50 – 200 mg/l and a N-Kj of 5 – 20 mg/l. Some components that can be found in this waste water are methanol (ethanol), ethers and formic acid (acetic acid).

Solid wastes generated

Waste generated is the spent catalyst/resin with no possibility of regeneration. Every two years, it should be changed and steamed to flare before recycling. The catalyst is recycled for recovery of its palladium content. Some efforts in the recycling of the resin have not been successful.

3.12 Gas separation processes

Consumption

The electricity demand of a gas separation process varies between 15 and 20 kWh per tonne of feedstock processed. These processes also consume between 300 and 400 kg of steam per tonne of feedstock and between 1 and 2 m³/t of cooling water ($\Delta T=10^{\circ}\text{C}$).

Emissions

Air emissions

Potential releases into air include hydrocarbons from pressure reliefs on vessels, regeneration vent gas from molecular sieves, C₁/C₂ refinery fuel gas, refrigeration system leaks, storage and handling operations. Mercury, if present in the feedstock of the refinery, will concentrate in overhead sections, particularly coolers. LPG, tops and naphtha coolers are most likely involved. Steaming this contaminated equipment may generate mercury emissions to atmosphere. Mercury is sometimes found upon opening equipment for inspection and maintenance.

The final process in LPG production is the addition of some odorants. The odorants used are typically volatile organic sulphur compounds, i.e. mercaptans and sulphides. Potential releases into air include leaks or spillages of odorant and vapours displaced during tank filling or from thermal expansion of blanket gas. They also include the displaced vapours residue post-incinerating or flaring if these techniques are used, including a small release of sulphur dioxide from combustion of the odorant.

Waste water

Potential releases into water include spillages of hydrocarbons, H₂S, NH₃ and amines.

Solid wastes generated

Potential releases into land include hydrocarbons from contaminated spent molecular sieves and from odorant addition including solid waste such as materials used to absorb odorant spillage.

3.13 Hydrogen-consuming processes

Consumption

In this section, two groups of processes have been included: hydrocracking and hydrotreatment. Both types of processes are catalytic and consume hydrogen. Table 3.62 shows the approximate hydrogen consumption for hydrotreatment and hydrocracking of various feedstocks.

Table 3.62: Hydrogen consumption data

| Process (Chemical consumption data) | % S w/w in crude | % S w/w in feed | Nm ³ of H ₂ per tonne of feed |
|---|---------------------|------------------------|--|
| Deep atmospheric residue conversion | 1 – 2 | 2 – 3.5 | 260 – 500 |
| Hydrocracking vacuum gas oil | 0.5 – 0.8 | 2 – 3 | 260 – 400 |
| Cycle oil hydrogenation | 0.3 | 3 | 370 |
| Hydrotreating | | | |
| FCC naphtha/coker naphtha | 0.05 – 0.01 | 1 | 110 |
| Kerosene | 0.1 – 0.02 | 0.1 | 11 |
| Straight-run naphtha | 0.01 | 0.05 | 4 |
| Hydrodesulphurisation | | | |
| FCC gas oil/coker gas oil | 0.1 | 1 | 130 |
| High-sulphur gas oil to 0.05 % S | 0.05 | 0.35 | 200 |
| High-sulphur gas oil to 0.2 % S | 0.04 | 0.3 | 44 |
| Low-sulphur gas oil to 0.05 % S | 0.04 | 0.15 | 17 |
| Low-sulphur gas oil to 0.2 % S | 0.03 | 0.1 | 13 |
| Hydroconversion | | Metal content <500 ppm | |
| <i>Source:</i> [175, Meyers 1997], [168, VROM 1999] | | | |

3.13.1 Hydrotreatment

Hydrotreatment units consumption

The H₂ consumption, and consequently the energy requirement, significantly increase in the order naphtha (0.05 % H₂), distillate (0.3 % H₂) and residue hydrotreating (1.8 % H₂). Table 3.63 shows the utility requirements for different hydrotreatments.

Table 3.63: Utility requirements for different hydrotreatments

| | Fuel (MJ/t) | Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, ΔT=10°C) | Wash water (kg/t) | H ₂ (kg/t) |
|--|----------------|------------------------|--------------------------|---|-------------------------|--------------------------|
| Naphtha processed | 200 – 350 | 5 – 10 | 10 – 60 | 2 – 3 | 40 – 50 | 1 – 15 |
| Distillate processed | 300 – 500 | 10 – 20 | 60 – 150 | 2 – 3 | 30 – 40 | 1 – 15 |
| Residue processed | 300 – 800 | 10 – 30 | 60 – 150 | 2 – 3 | 30 – 40 | 10 – 100 |
| <i>Sources:</i> [151, Sema, Sofres 1991], [168, VROM 1999] | | | | | | |

Table 3.64: Catalysts used in hydrotreatments

| Process | Composition | Cycle lengths/average consumption (t/Mt feedstock) |
|-------------------------------------|--|--|
| Hydrodesulphurisation | CoO/MoO ₃ /Al ₂ O ₃ | 1 year/46 |
| Denitrification | Ni/Mo catalyst | 2 – 6 years/46 |
| Demethalisation | NA | <1 year/NA |
| Saturation of olefins and aromatics | Ni/Mo catalyst | 1 year/NA |
| Hydrogenation of light dienes | NA | 2 years/NA |

Emissions from hydrotreatment units*Emissions to air*

Air emissions from hydrotreating may arise from process heater flue-gas (dealt with in Section 3.10), vents, fugitive emissions and catalyst regeneration (CO₂, CO, NO_x, SO_x). The off-gas stream may be very rich in hydrogen sulphide and light fuel gas. The fuel gas and hydrogen sulphide are typically sent to the sour gas treatment unit and sulphur recovery unit. Hydrocarbons and sulphur compounds may be emitted to air from pressure relief valves; leakages from flanges, glands and seals on pumps, compressors and valves, particularly on sour gas and sour water lines; venting during catalyst regeneration and replacement procedures or during cleaning operations. Table 3.65 shows two examples of emissions from hydrotreating processes. These air emissions include the emissions generated by the combustion of fuel required in these processes.

Table 3.65: Examples of air emissions generated by hydrotreatment units

| Installation OMV Schwechat(*) (2007) | Fuel consumption (GWh/yr) | Throughput (t/yr) | Units | SO ₂ | NO _x | CO | CO ₂ | Particulates |
|---|---------------------------------|----------------------|-------------------|----------------------|-----------------|-------|-----------------|--------------|
| Naphtha hydrotreater | | 1 160 000 | mg/m ³ | 700 (¹) | 74 | 10 | | 20 |
| | 205.9 | Naphtha | t/yr | 142 | 15 | 2 | 40 152 | 4.1 |
| | | | kg/t feed | 0.13 | 0.013 | 0.002 | 36 | 0.004 |
| Middle distillate | | 1 780 000 | mg/m ³ | 59 | 242 | 5 | | 1 |
| | 135.8 | Kerosene. GO | t/yr | 8.1 | 33 | 0.7 | 26 341 | 0.1 |
| | | | kg/t feed | 0.005 | 0.019 | 0 | 15 | 0 |
| Vacuum distillate | | 1 820 000 | mg/m ³ | 700 (1) | 442 | 10 | | 20 |
| | 72.4 | VGO | t/yr | 51.6 | 32.6 | 0.7 | 19 466 | 1.5 |
| | | | kg/t feed | 0.028 | 0.018 | 0 | 10.7 | 0.001 |

(¹) Raw gas was treated in a flue-gas desulphurisation (Wellman-Lord).
Data are related to yearly average, 3 % O₂, dry conditions.
(*) Since 2010, the Schwechat refinery (AT) uses only gas (except for the SNO_x power plant unit) with the following daily average emissions: SO₂: 1 – 20 mg/Nm³, NO_x: <100 mg/Nm³, CO: <80 mg/Nm³, PM: 1 mg/Nm³.
Source: [194, Winter 2000] updated TWG-AT 2010

| Installation TOTAL Mitteldeutsche land | Fuel consumption (GWh/yr) | Throughput (t/yr) | Units | SO ₂ | NO _x | CO | CO ₂ | Particulates |
|---|---------------------------------|----------------------|-------------------|-----------------|-----------------|-------|-----------------|--------------|
| Naphtha hydrotreater | | 1 500 000 | mg/m ³ | 35 | 100 | 100 | | 5 |
| | 205.9 | Naphtha | t/yr | 7.1 | 20.3 | 20.3 | 39 937 | 1 |
| | | | kg/t feed | 0.005 | 0.014 | 0.014 | 27 | 0.001 |
| Middle distillate | | 3 000 000 | mg/m ³ | 35 | 100 | 100 | | 5 |
| | 205.9 | GO | t/yr | 7.1 | 20.3 | 20.3 | 39937 | 1 |
| | | | kg/t feed | 0.002 | 0.007 | 0.007 | 13 | 0 |
| Vacuum distillate | | 2 600 000 | mg/m ³ | 35 | 100 | 100 | | 5 |
| | 578.2 | VGO | t/yr | 18.6 | 53.2 | 53.2 | 164 776 | 2.7 |
| | | | kg/t feed | 0.007 | 0.02 | 0.02 | 63 | 0.001 |

NB: Emissions are only limit values. Loads and specific emissions were calculated.
Data are related to yearly average, 3 % O₂, dry conditions.

Waste water

Hydrotreating and hydroprocessing generate a flow of waste water of 30 – 55 l/tonne. The waste water contains H₂S, NH₃, phenols, hydrocarbons, suspended solids, BOD and COD, and has a high pH and should be sent to the sour water stripper/treatment. Potential releases into water include HC and sulphur compounds from spillages and leaks, particularly from sour water lines. In distillate hydrotreatments, solid deposits such as (NH₄)₂SO₄ and NH₄Cl are formed in the cooler parts of the unit and must be removed by water wash.

Solid wastes generated by hydrotreatments

These processes generate spent catalyst fines (aluminium silicate and metals Co/Mo and Ni/Mo: 50 – 200 t/yr for a 5 Mt/yr refinery). For process units using expensive catalysts, contracts with the supplier exist for taking the spent catalyst back for regeneration and/or recycling. This practice is also being adopted for other types of catalysts. The use of catalytic processes has increased considerably and hence also the regeneration and rework services, particularly for Ni/Mo and Co/Mo hydrotreating catalysts. Molecular sieve beds are sometimes used to capture the water content of some streams (e.g. distillate hydrodesulphurisation).

3.13.2 Hydrocracking

Consumption of hydrocracking units

Hydrocracking is an exothermic process. The heat generated in the reactors is partially recovered in a feed/product heat exchanger. A significant amount of heat is required in the fractionation section. Catalysts used in this process are typically cobalt, molybdenum, nickel or tungsten oxides impregnated on alumina. Fluorided alumina, activated clay, silica-alumina or zeolites are also present. Average consumption of catalysts is 57.4 t/Mt of feedstock. A small amount of coke-like material is formed which accumulates over time on the catalyst. This deactivates the catalyst, requiring regeneration off site every one to four years by burning off the coke. Water is removed by passing the feed stream through a silica gel or molecular sieve dryer. The utility requirements for hydrocracking are shown in Table 3.66.

Table 3.66: Utility consumption of hydrocracking units

| | Fuel (MJ/t) | Electricity (kWh/t) | Steam produced (kg/t) | Cooling water (m ³ /t, $\Delta T=17\text{ }^{\circ}\text{C}$ (* $\Delta T=10\text{ }^{\circ}\text{C}$)) |
|-----------------|----------------|------------------------|--------------------------|--|
| Hydrocracking | 400 – 1200 | 20 – 150 | 30 – 300 | 10 – 300 |
| Hydroconversion | 600 – 1000 | 50 – 110 | 200 – 300 | 2 – 10 |

Source: [151, Sema, Sofres 1991], [168, VROM 1999]

Emissions from hydrocracking units

Emissions to air

Heater stack gas contains CO, SO_x, NO_x, hydrocarbons and particulates that generate smoke, grit and dust in flue-gas (covered in Section 2.10), fugitive emissions (hydrocarbons) and catalyst regeneration emissions (CO₂, CO, NO_x, SO_x, and catalyst dust). Fuel gas and bleed stream will contain H₂S and should be further treated. VOCs are generated by the non-condensables from vacuum ejectors.

Waste water

Hydrocracking generates a flow of waste water of 50 – 110 litres per tonne processed. It contains high COD, suspended solids, H₂S, NH₃ and relatively low levels of BOD. The sour water from the first stage HP separator, LP separator, and overhead accumulator should be sent to the sour water stripper/treatment. Effluents from hydroconversion processes may occasionally contain metals (Ni/V).

Solid wastes

Hydrocracking also generates spent catalyst fines (metals from crude oil, and hydrocarbons). Catalyst should be replaced once every one to three years, generating an average of 50 – 200 t/yr for a refinery of 5 Mt/yr. Hydroconversion normally generates between 100 and 300 t/yr of spent catalysts which contain more heavy metals than hydrocracking catalysts.

3.14 Hydrogen production

Consumption

Steam reforming

The steam reformer has to supply a large amount of heat at high temperature for the steam reforming reaction by burning fuel. Global fuel consumption of a unit includes the one for hydrogen production plus that associated with steam export to nearby installations.

Fuel requirement values indicated in Table 3.67 are those strictly associated with hydrogen production. They refer to large size equipment (50 000 Nm³/h of H₂ or more). Achieving such values requires both the use of the technique described further in Section 4.14.1 (preheating feed process, steam superheating, combustion air preheating) and the use of the PSA separation process in order to recover energy contained in by-products, mainly CO and CH₄, and feed it back to burners (up to 90 % recovery of the required energy for steam reforming).

As more and more steam is produced and exported, total energy requirements can be higher.

Values of the electricity requirement do not include product compression. Also, the cooling for such compressors is not included in the values presented for the cooling water utility.

Table 3.67: Utility requirements for steam reforming (large sized recent equipment)

| Fuel (MJ/t H ₂) | Electricity (kWh/t) | Steam produced (kg/t) | Cooling water (m ³ /t, ΔT=10 °C) |
|--|---------------------|-----------------------|---|
| 20 000 – 30 000 | 200 – 400 | 2 000 – 8 000 | 25 – 100 |
| <i>Source: [151, Sema, Sofres 1991], TWG 2010 (EIGA)</i> | | | |

On average, these processes produce 3 000 – 3 600 Nm³ of hydrogen (240 – 310 kg) per tonne of feedstock. The catalyst for reforming is 25 – 40 % nickel oxide deposited on a low-silica refractory base. The catalyst used in the reformer furnace is not regenerable and is replaced every four or five years. Longer lifetimes can be achieved when the feed is light, such as CH₄, of constant quality and the catalyst is well sulphur-protected. Lifetime doubling may be achieved, especially when desulphurised feed is first fed to a pre-reformer unit installed upstream of the reformer.

The composition of the product depends on the purification technique, as shown in Table 3.68.

Table 3.68: Composition of the hydrogen product in steam reforming

| Parameter | Wet scrubbing technique | Pressure swing adsorption |
|-------------------------------------|-------------------------|---------------------------|
| Hydrogen purity, % v/v | 95 – 97 | 99 – 99.99 |
| Methane, % v/v | 2 – 4 | 100 ppm v/v |
| CO+CO ₂ , ppm v/v | 10 – 50 | 10 – 50 |
| Nitrogen, % v/v | 0 – 2 | 0.1 – 1.0 |
| <i>Source: [175, Meyers 1997]</i> | | |

Coke gasification

Coke gasification produces between 2 600 and 3 500 Nm³ of hydrogen (210 – 300 kg) per tonne of gasified coke. Figure 3.35 shows a scheme of the hydrogen production from a coke gasifier and the amount of hydrogen produced per tonne of petroleum coke.

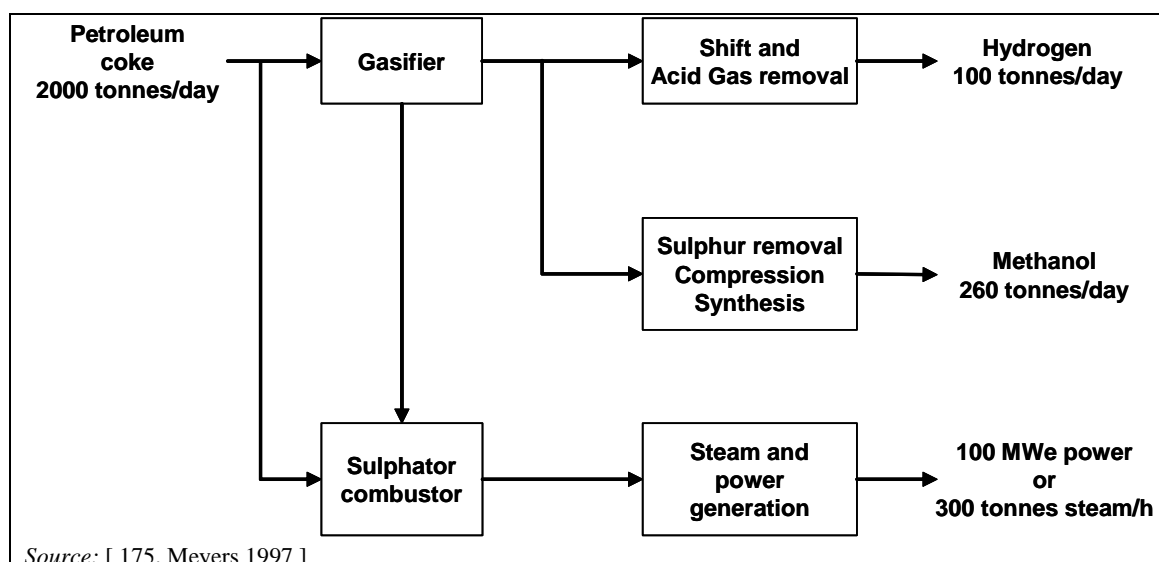


Figure 3.35: Petroleum coke commercial process

Heavy fuel gasification

Bitumen and heavy fuel can be gasified. The bitumen used in the gasification has the characteristics that are shown in Table 3.69.

Table 3.69: Characteristics of bitumen used as partial oxidation feedstock

| Parameter | Typical value | Unit |
|------------------|---------------|-------|
| Density at 15 °C | 1.169 | kg/l |
| Carbon | 85.05 | % w/w |
| Hydrogen | 8.10 | % w/w |
| Nitrogen | 0.80 | % w/w |
| Sulphur | 6.00 | % w/w |
| Ash | 0.05 | % w/w |
| Vanadium | 600 | ppm |
| Nickel | 200 | ppm |

Source: [175, Meyers 1997]

Air emissions

Steam reforming

NO_x emissions are the most important to consider. Other emissions such as SO_x or water emissions are minimal, because low-sulphur fuel is typically used and there are few emissions other than flue-gas. The choice of heat recovery system can have a major effect on NO_x production, since both the amount of fuel fired and the flame temperature will be affected. NO_x emissions from a steam reforming unit using gas or light gasoline as fuels and with low-NO_x burners are 25 – 40 mg/MJ (100 – 140 mg/Nm³, 3 % O₂) [160, Janson 1999]. In case air is preheated, those values reach up to 200 mg/Nm³ (3 % O₂) [56, EIGA 2009]. Other emissions, such as CO₂, originate from carbon in the feed.

Coke gasification

Sulphur sorbents, such as limestone (CaCO₃) or dolomite (Mg, Ca carbonate), are normally used in the gasifier, drastically reducing the sulphur content. Sulphur composition in the exhaust gas ranges from 600 to 1 200 mg/Nm³ of H₂S and COS. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. In oxygen-blown gasification, the sulphur content will be about 10 000 mg/Nm³ per unit of % sulphur in the feed. Ammonia is

formed in the gasifier from the fuel-bound nitrogen. Ammonia in the product gas typically contains less than 5 % of the fuel-bound nitrogen when limestone is present in the gasifier.

Heavy fuel gasification

For the TOTAL Mitteldeutschland refinery, data are available concerning air emissions of the partial oxidation unit and are given in Table 3.70.

Table 3.70: Example of air emissions generated by heavy fuel gasification

| Fuel consumption (GWh/yr) | Throughput (t/yr) | Units | SO ₂ | NO _x | CO | CO ₂ | Particulates |
|--|-------------------|-------------------|-----------------|-----------------|-------|-----------------|--------------|
| 2452.8 | 670000 | mg/m ³ | 35 | 158 | 100 | | 5 |
| | | t/yr | 243.4 | 1099 | 695.5 | 475 843 | 34.8 |
| | | kg/t feed | 0.363 | 1.64 | 1.038 | 710 | 0.052 |
| NB: For the emissions, only limit values are given. Loads and specific emissions were calculated. Data are related to yearly average, 3 % O ₂ , dry conditions. Source: [191, UBA Austria 1998] | | | | | | | |

Solid waste

Coke gasification

The solid waste from the process consists mainly of spent limestone and metals from the pet coke. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm. Volatile metals and alkalis tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burnt and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in the subsequent processing of the gas. The solid waste from the process consists mainly of spent limestone and metals from the pet coke. After processing in the combustor/sulphator, this material is sent to disposal. Vanadium and nickel are found in most petroleum cokes in concentrations far greater than in coals or lignites. They remain in the ash product.

3.15 Integrated refinery management

Emissions in abnormal circumstances

Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard. Emergency situations are normally regulated in the refinery permit. Quantification of these emissions is difficult.

Start-up and shutdown

Conditions such as start-up and shutdown operations occur fairly infrequently and are normally of short duration. Modern designs include fully automated fail-safe start-up and shutdown systems with interlocks to maximise safety and to minimise risk and emissions. Start-up and shutdown of a full refinery or part of the installation may result in substantial emissions to atmosphere, mainly VOC, SO₂, CO₂ and particulates. Effluent drainage and treatment facilities could also be temporarily overloaded. Refinery design and operational constraints call for safe and environmentally acceptable management and disposal of emissions, discharges and waste in upset conditions. Start-up and shutdown procedures, and hence emissions and discharges, vary according to the type of unit and the purpose of the shutdown. If a particular unit is only to be depressurised and heavy components flushed out for a temporary stop, the emissions will be far less than if all equipment must be purged, steamed out and filled with air to allow workers to enter. Stringent safety and health care procedures are normal practice in present-day refineries. Not only personnel but also contractors have to adhere to these procedures. Nevertheless, occasional accidents take place and safety precautions should be practised regularly. Shutdown or blowdown can also have an impact on neighbouring dwellings (noise and light flaring).

Heat exchangers cleaning

The bundles of heat exchangers are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities. The sludge generated (oil, metals and suspended solids) may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents. Oily waste water is also generated during heat exchanger cleaning. VOC emissions may occur during these processes.

Utilities management

Water management

Surface water run-off is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Run-off surface water also includes water coming from crude and product storage tank roof drains.

The daily sanitary waste water production of an individual is about 120 litres, so the total sanitary effluent of the refinery can be easily calculated. Normally this domestic effluent is collected in a septic tank and then treated in the waste water treatment plant.

Ballast water is relevant to these refineries that have crude receipt facilities or handle large product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and heavily polluted with oil. It can easily lead to an upset of existing effluent treatment systems. The use of ballast water tanks is therefore an important equalisation tool for feeding the water in a controlled way to either the process water system or the continuously oil-contaminated system, if the COD is lower than 100 ppm. As more and more tankers are equipped with segregated ballast tanks, the ballast water problem is slowly phasing out.

Water used in processing operations also accounts for a significant portion of the total waste water. Process waste water arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Because process

water often comes into direct contact with oil, it is usually contaminated and requires adequate treatment before reuse or discharging.

The water usage depends both on the purpose and complexity of the refinery. While there are usually opportunities to economise on water use, the scope for major reductions in existing refineries is sometimes limited. The CONCAWE 2010 survey (100 refineries) reports the following data on water usage (annual data).

| | | |
|---|--------------|---------------------|
| Annual median total fresh water intake: | 5.7 | Mm ³ /yr |
| Range (5th – 95th percentile): | 0.4 to 220 | Mm ³ /yr |
| Annual median fresh water: | 3.7 | Mm ³ /yr |
| Range (5th – 95th percentile): | 0.14 to 37.8 | Mm ³ /yr |
| Annual median fresh water per tonne throughput: | 0.70 | m ³ /yr |
| Range of fresh water per tonne throughput: | 0.1 to 8.6 | m ³ /yr. |

The recorded fresh water consumption is that taken from:

- potable (mains) water;
- river water;
- privately extracted groundwater (including in some cases contaminated groundwater extracted for purposes of treatment).

It does not include:

- recycled final effluent;
- storm water;
- ballast water from ships;
- waste water from adjoining facilities;
- seawater.

Blowdown systems

The gaseous component of the blowdown system typically contains hydrocarbons, hydrogen sulphide, ammonia, mercaptans, solvents and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons, in the case of direct discharge to the atmosphere, and sulphur oxides, when flared. The liquid is typically composed of mixtures of water and hydrocarbons containing sulphides, ammonia and other contaminants, which are sent to the waste water treatment plant.

A seal drum blowdown generates an effluent of 1 – 2 m³/h and 10 times as much in the case of an emergency, with a composition of (analysis of water seal after e.g. visbreaker start-up):

- COD: 500 – 10 000 mg/l;
- H₂S: 10 – 1 000 mg/l;
- NH₃: 10 – 1 000 mg/l.

3.16 Isomerisation

The main environmental problems for isomerisation, apart from the energy consumption, are the catalyst promotion and the possible side effects.

Consumption

The total energy requirement depends mainly on the isomerisation catalyst technology used, the configuration including for the hydrogen recycle, the hydrocarbon recycle operation (2 – 2.5 times higher than once-through), and the technology used to separate the n- from the iso-paraffins; absorption/desorption process or a deisohexaniser column. The isomerisation processes require an atmosphere of hydrogen to minimise coke deposits. The utility requirements for the isomerisation processes vary widely depending on the design options. An example of the utility requirements for an isomerisation process is shown in Table 3.71:

Table 3.71: Utility requirements of the isomerisation processes

| Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, ΔT=10 °C) |
|---------------------|-----------------------|---|
| 20 – 30 | 300 – 600 | 10 – 15 |

Catalyst life can range from two to more than ten years depending on unit operation. The chloride-promoted catalyst (chlorinated alumina containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activity, to avoid catalyst deactivation and potential corrosion problems. See Section 2.16 for further information about the type of catalysts used.

Table 3.72 shows the utility and chemical requirements for the adsorption process for a feed rate of 600 tonnes per day.

Table 3.72: Utilities and chemical requirements of an adsorption process

| Utilities and chemical requirements of the adsorption process | |
|---|-------|
| Fuel consumed (90 % furnace efficiency), MW | 9 |
| Water (ΔT = 17 °C), m ³ /day | 2 159 |
| Power, kWh | 1 455 |
| Steam at 10.5 kg/cm ² , saturated, kg/h | 2.8 |
| Hydrogen consumption, Nm ³ /day | 17.7 |
| Soda consumption, kg | 8.4 |
| Hydrogen chloride, kg | 6 |
| Catalyst consumption, kg | 0.12 |
| <i>Sources: [175, Meyers 1997], [241, O. G. Journal 2000]</i> | |

Emissions

Air emissions

Air emissions may arise from the process heater (used in some designs), vents and fugitive emissions. Other emissions are HCl (potentially in light ends from organic chloride added to maintain the catalyst activity), from vents and fugitive emissions, pressure reliefs on surge drum, separators and column reflux drum, regeneration vent gas from dryers, storage and handling operations and spillage (hydrocarbons). Releases of hydrogen may occur from pressure relief on the hydrogen system. Product stabilisation, however, does result in small amounts of LPG (C₃+C₄, rich in i-C₄) and in stabiliser vent (H₂+C₁+C₂) products. The stabiliser

vent products are usually used as refinery fuel. In the chloride alumina catalyst isomerisation design, fuel gas is normally caustic-treated to remove HCl.

Process waste water

Potential releases into water include hydrocarbons from the reflux drum boot drain and spillages. With the chlorided alumina isomerisation catalyst design, additional waste water is generated by spent sodium hydroxide from the scrubber system. In this design, the process waste water contains chloride salts, caustic wash, traces of H₂S and NH₃ and has a high pH. Brine from the feed dryer (desiccant, water free CaCl₂) contains dissolved CaCl₂ and hydrocarbons. Its flow depends on moisture content and is usually drained to the effluent treatment plant.

Residual wastes generated

Potential releases to land include hydrocarbons from spillages/contaminated molecular sieves and catalyst. Calcium chloride sludge (or other desiccants) is the waste generated in this process. The catalyst used in these processes is normally regenerated by the catalyst manufacturers. Mainly platinum is then recovered from the used catalyst off site. Molecular sieves can be used as feed drying agent. The flow and composition are plant-specific and the spent molecular sieves are disposed of as non-regenerable solid waste.

3.17 Natural gas plants

Consumption

Water and energy consumption within natural gas plants is shown in Table 3.73.

Table 3.73: Example of utility consumption in natural gas plants (Norway)

| Water and energy consumption | Existing plant (Kårstø Plant) | New plant (Ormen Lange Plant at Nyhamna)([⊙]) |
|--|--|---|
| Capacity | 88 million Nm ³ /day of rich gas 840 t/h unstabilised condensate | 70 million Nm ³ /day export gas 8 400 Nm ³ /day condensate |
| Fuel gas | 60 tonnes/h at full capacity | 8 tonnes/h |
| Power (gas power)) | 775 MW | 2 x 42.1 MW installed |
| Water (steam production) | 60 m ³ /h | NA |
| Seawater cooling | 44 000 m ³ /h | 14 400 Nm ³ /h (Energy flux ~160 MW for normal operations) |
| [⊙] Norske Shell operates the gas plant at Nyhamna for the processing of gas and condensate from the Norwegian offshore Ormen Lange gas field. Source: [217, Statoil 2000] Updated TWG NO 2010 | | |

Emissions

Emissions to air

The major emission sources in the natural gas processing industry are compressors, boilers and furnaces, acid gas wastes, fugitive emissions from leaking process equipment and, if present, glycol dehydrator vent streams. Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethylbenzene and xylene, as well as a wide range of less toxic organics.

Potential release routes for prescribed substances and other substances which may cause harm are shown in Table 3.74.

Emissions of SO₂ will result from gas sweetening plants only if the acid waste gas from the amine process is flared or incinerated. Most often, the acid waste gas is used as a feedstock in nearby sulphur recovery (see Section 4.23.5.2) or sulphuric acid plants. When flaring or incineration is practised, the major pollutant of concern is SO₂. Most plants employ elevated smokeless flares or tail gas incinerators for complete combustion of all waste gas constituents, including virtually 100 % conversion of H₂S to SO₂. Little results from these devices in the way of particulates smoke or hydrocarbons and, because gas temperatures do not usually exceed 650 °C, no significant quantity of nitrogen oxides is formed. Emission factors for gas sweetening plants with smokeless flares or incinerators are presented in Table 3.75. Factors are expressed in units of kilograms per 1 000 cubic metres. Emission data for sweetening processes other than amine types are very meagre, but a sulphur mass balance will give accurate estimates for sulphur dioxide (SO₂).

Table 3.74: Releases to the environment commonly associated with the natural gas processes

| Type of process | H ₂ S | SO ₂ | NO _x | CO, CO ₂ | Organic compounds | Oily waters | N ₂ | Spent catalysts/ adsorbents | Sand/ corrosion products | Acids/ alkalis/ salts, etc. |
|-------------------------|------------------|-----------------|-----------------|---------------------|-------------------|-------------|----------------|-----------------------------|--------------------------|-----------------------------|
| Onshore reception | A(*) | | | | AW | W | | | L | |
| Gas treatment processes | A(*) | | A | A | AW | W | | L | | L |
| Acid gas processes | A(*) | A(*) | A | A | AW | W | | L | | |
| Nitrogen removal | A(*) | | | | A | | A | | | |
| Hydrocarbon removal | | | | | AW | W | | | | |
| Gas compression | | | A | A | A | | | | | |
| Condensate treatment | | | A | A | AW | | | L | | W |
| Field water treatment | | | | | W | W | | | | |
| Flares/vents | A(*) | A(*) | A | A | A | | | | | |
| Gas storage sites | A | A | A | A | AW | W | | L | | |

(*) If sour gas is being processed.
 NB: A: air, W: water, L: land.
 Source: [173, HMIP UK 1997]

Table 3.75: Emission factors for gas sweetening plants

| Amine process | kg/10 ³ Nm ³ gas processed | Comments |
|---------------------------------------|--|--|
| Particulate | Negligible | |
| SO _x (as SO ₂) | 26.98 | Assumes that 100 % of the H ₂ S in the acid gas stream is converted to SO ₂ during flaring or incineration and that the sweetening process removes 100 % of the H ₂ S in the feedstock. |
| | 0.408(*) | For an emission ratio of 0.75 % |
| | 0.272(*) | For an emission ratio of 0.50 % |
| CO | 0.25(*) | |
| Hydrocarbons | - | Flares or incinerator stack gases are expected to have negligible hydrocarbon emissions. |
| NO _x | Negligible | |

Sources: (*) [172, MRI 1997], [54, Gallauner et al.2009]

Emissions to water

Routine process-derived liquid effluent produced by natural gas plants is normally derived mainly from water arising from the drying of the gas and associated condensate. The effluent principally occurs as condensed steam from the glycol or methanol regeneration plants and usually contains a number of organic contaminants, including glycol, methanol, aliphatic and aromatic hydrocarbons, amines and mercaptans. The presence of these contaminants typically causes the effluent to have a very high biochemical and chemical oxygen demand. The process of refining natural gas which contains mercury can generate waste water which contains that metal.

Solid waste

Natural gas refining gives rise to relatively small quantities of process wastes. These typically include occasional disposal of spent catalysts, activators, corrosion inhibitors, absorbents,

adsorbents, filter cartridges, separator dusts, etc. and they may be contaminated with trace amounts of hydrocarbons. Some natural gas sources contain traces of Hg which should be collected (generating spent adsorbent) and safely disposed of. For every 1 000 kg of sludge treated, 12 kg of metallic mercury is produced. Total sludge production within some Dutch natural gas plants is on average 250 tonnes/yr, with a maximum of 400 tonnes/yr. This corresponds to 3 – 5 tonnes of mercury annually.

3.18 Polymerisation

Consumption

The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. Typically 0.2 grams of phosphoric acid are consumed to produce 1 tonne of polymer or 1.18 kg of catalyst (phosphoric acid + support) per tonne of product. Catalyst life is normally limited from three to six months, depending on unit size and operating conditions. A typical unit, capable of producing 25 tonnes of polymerised gasoline per day, is customarily filled with 12 tonnes of catalyst.

Caustic solution is used to remove mercaptans from the propene/butene feed, followed by amine solution to remove hydrogen sulphide, then, water to remove caustics and amines. It is finally dried by passing through a silica gel or molecular sieve dryer.

Table 3.76 shows the typical utility consumption of a polymerisation process.

Table 3.76: Utility consumption in polymerisation process

| Utility | Consumption | Unit |
|-------------------------------------|-------------|-----------------|
| Electric power | 20 – 28 | kW/t of product |
| Steam | 0.7 – 1.1 | t/t of product |
| Cooling water | 4.4 – 6.0 | t/t of product |
| <i>Source: [175, Meyers 1997]</i> | | |

Emissions

Emissions to air

Potential releases into air include hydrocarbons from pressure reliefs, storage and handling operations, spillages and water and waste discharges, and of particulate matter from catalyst fines, from handling and disposal of spent catalysts. Sulphur dioxide and H₂S may arise during the caustic washing operation.

Process waste water

Potential releases into water include hydrocarbons from sour water purge from the wash tower, condenser drains and spillages, and of particulate matter from spillages of catalyst fines. Waste water streams will contain caustic wash and sour water with amines and mercaptans. The most important parameters are H₂S, NH₃, caustic wash, mercaptans and ammonia, and low pH (2 – 3) due to the phosphoric acid.

Solid waste generated

Spent catalyst containing phosphoric acid, which typically is not regenerated, is occasionally disposed of as a solid waste. Potential releases into land include acids in solid form and hydrocarbons from spent catalyst. Typically, 0.4 grams of used silica are disposed of per tonne of polymer gasoline produced.

3.19 Primary distillation units

Consumption

Despite the high level of heat integration and heat recovery that is normally applied, crude distillation units (CDU) are among the most intensive energy-consuming units in a refinery, because the total volume of crude oil being processed has to be heated to the elevated processing temperature of 350 °C. The overall energy consumption of a refinery is normally dominated by a few processes. Atmospheric and vacuum distillation account for 35 – 40 % of the total process energy consumption, followed by hydrotreating with approximately 18 – 20 % [177, WRA 1999]. The various processes downstream of the CDU make use of the elevated temperatures of the product streams leaving the CDU. The number of side-streams in a high vacuum unit is chosen to maximise heat integration of producing streams at different temperatures, rather than to match the number of products required. The utility requirements for the atmospheric and vacuum distillation units are shown in Table 3.77.

Table 3.77: Utility requirements for atmospheric and vacuum distillation units

| Type of unit | Fuel (MJ/t) | Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, ΔT = 17 °C) |
|--------------|-------------|---------------------|-----------------------|---|
| Atmospheric | 400 – 680 | 4 – 6 | 25 – 30 | 4.0 |
| Vacuum | 400 – 800 | 1.5 – 4.5 | 20 – 60 | 3 – 5 |

NB: Replacement of the steam ejectors by vacuum pumps will reduce steam consumption and waste water generation but increase the electricity consumption.
Sources: [168, VROM 1999], [204, Canales 2000], [207, TWG 2001]

Emissions

Air emissions

Potential releases into air are from:

- Flue-gases arising from the combustion of fuels in the furnaces to heat the crude oil.
- Pressure relief valves on column overheads; relief from overhead accumulators are piped to flare as well as the vent points.
- Poor containment in overhead systems, including barometric sumps and vents.
- Glands and seals on pumps, compressors and valves.
- Decoking vents from process heaters. During furnace decoking (once or twice a year), some emission of soot can occur if the operation is not properly controlled in terms of temperature or steam/air injection.
- Venting during clean-out procedures.
- Some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of non-condensable light hydrocarbons and hydrogen sulphide passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide. The quantity of these emissions depends on the size of the unit, the type of feedstock and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated. Oily sour water is also generated in the fractionators. The emissions of non-condensables from vacuum ejector set condensers are between 50 and 200 kg/h, depending on furnace design and type of crude and throughput. They include hydrocarbons and H₂S.
- Fugitive emissions from atmospheric and vacuum distillation units account for 5 –190 t/yr for a refinery with a crude capacity of 8.7 Mt/yr [155, API 1993].

Table 3.78 gives some examples of the air emissions generated by the atmospheric and vacuum distillation units of two European refineries. This table includes the emissions from combustion of fuels in the furnaces.

Table 3.78: Examples of air emissions generated by crude oil and vacuum distillation units

| Installation | Fuel consumption (GWh/yr) | Throughput (t/yr) | Units | SO ₂ | NO _x | CO | CO ₂ | Particulates |
|--|---------------------------|-------------------|-------------------|-----------------|-----------------|-------|-----------------|--------------|
| CDU TOTAL Mittel Deutschland | | 8 500 000 | mg/m ³ | 35 | 100 | 100 | | 5 |
| | 1 138.8 | Crude oil | t/yr | 35.2 | 100.4 | 100.4 | 220 927 | 5 |
| | | | kg/t feed | 0.004 | 0.012 | 0.012 | 26 | 0.001 |
| Vacuum distillation TOTAL Mittel Deutschland | | 4 500 000 | mg/m ³ | 35 | 100 | 100 | | 5 |
| | 639.5 | Atm. Res. | t/yr | 19.8 | 56.6 | 56.6 | 182 252 | 2.8 |
| | | | kg/t feed | 0.004 | 0.013 | 0.013 | 41 | 0.001 |

(¹) Raw gas was treated in a flue-gas desulphurisation (Wellman-Lord).
 NB: Data are related to yearly average, 3 % O₂, dry conditions.
 For the emissions from the TOTAL Mitteldeutschland refinery, only limit values are given. Loads and specific emissions are calculated.
 Source: [194, Winter 2000]

Process waste water

Process waste water generated in the atmospheric distillation units is 0.08 – 0.75 m³ per tonne of crude oil processed. It contains oil, H₂S, suspended solids, chlorides, mercaptans, phenol, an elevated pH, and ammonia and the caustic soda used in column overhead corrosion protection. It is generated in the overhead condensers, in the fractionators, and can also become contaminated from spillages and leaks. The overhead reflux drum (gas oil dryer condensator) generates 0.5 % water on crude + 1.5 % steam on feed, with a composition of 10 – 200 mg/l H₂S and 10 – 300 mg/l NH₃. Sour water is normally sent to water stripper/treatment.

Waste water (sour water) is generated in the vacuum distillation units from process steam injection in the furnace and the vacuum tower. It contains H₂S, NH₃ and dissolved hydrocarbons. If steam ejectors and barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated (± 10 m³/h) containing also H₂S, NH₃.

Residual wastes generated

Sludges can be generated from the cleaning-out of the columns. The amount depends on the mode of desludging and the base solid and water content of the crude processed. The range of solid waste generation from a crude unit of 8.7 Mt/yr ranges from 6.3 – 20 t/day.

3.20 Product treatments

Consumption

Gasoline sweetening

Utility requirements in a gasoline sweetening process are shown in the table below.

Table 3.79: Typical utility consumption of a gasoline sweetening process

| Electricity (kWh/t) | Steam consumed (kg/t) | Caustic (kg/t) |
|---|--------------------------|-------------------|
| 1 – 10 | 10 – 25 | 0.02 – 0.15 |
| <i>Sources: [204, Canales 2000], [168, VROM 1999], [175, Meyers 1997]</i> | | |

Catalytic dewaxing

Catalytic dewaxing catalysts typically last six to eight years. During that time, they are regenerated as needed. Typical cycles last two to four years between regenerations. Utilities needed in the catalytic dewaxing process are summarised in the following table.

Table 3.80: Typical utility consumption of catalytic dewaxing units

| Utilities for a feed capacity of 3 500 tonnes per stream day | |
|---|---------|
| Power, kW | 5 100 |
| Steam (tracing only) | Minimal |
| Cooling water, m ³ /h | 80 |
| Condensate, m ³ /h | 4 |
| Fuel absorbed, MW | 23 084 |
| <i>Source: [175, Meyers 1997]</i> | |

Emissions

Air emissions

Potential releases into air from oxidation-extraction processes include hydrocarbons, sulphur compounds (e.g. disulphides); and nitrogen compounds from sour water drains, pressure relief valves, vents from feed vessels, spillages and leakages from flanges, glands and seals on pumps and valves – particularly from overhead systems and fugitive emissions. Emissions may occur from the spent air from the disulphide separator that contains less than 400 ppm of disulphides and is normally incinerated.

Process waste water

Product treating processes do not generate much waste water. The potential releases into water are from spillages and leakages (hydrocarbons), and the sulphur and nitrogen compounds arising from inadequate stripping performance.

Residual wastes generated

In the extraction process, an oily disulphide waste stream leaves the separator. Most refineries are able to regenerate their spent caustic, but sometimes they have to dispose of some excess quantities of spent caustic, mainly from caustic prewash activities. Usually these quantities are small and can be managed within their effluent treatment system or they are disposed of externally via contractors or may be reused elsewhere. From the extraction process, the disulphide recovered can be sold as product, or recycled to a hydrotreater or incinerator. The amount of spent caustic generated varies between 0.05 and 1.0 kg/tonne feed and contains sulphides and phenols. The concentration of organic compounds in spent caustic solutions is typically higher than 50 g/l.

Table 3.81: Typical emissions from the catalytic dewaxing process

| Catalytic dewaxing process | | |
|---|-------------|---|
| Air | Waste water | Solid wastes |
| Flue-gas from fired heater. VOCs may arise from venting during catalyst regeneration/replacement procedures and cleaning. | None | Potential releases into land are from disposal of spent catalytic dewaxing catalyst (50 t/yr for a 50 000 t/yr hydrofining process). Spent Ni-W catalysts containing sulphur and carbon sent to specialised off-site regeneration companies. After two to three regenerations, catalyst is disposed of and subjected to metal reclaiming. |

3.21 Storage and handling of refinery materials

Consumption

No energy or process material is required for balancing lines, double seals or floating roofs on tanks. However, some tanks need mixers (a heavy user of power) and some need heating too. Handling refinery materials also requires electricity for the pumps that move the materials through the pipes.

Emissions

Air emissions

Air emissions, and more specifically VOC emissions, are the main emissions that occur during the storage and handling of refinery materials. Emissions from hydrocarbon liquids in storage occur because of evaporative loss of the liquid during storage and as a result of changes in the liquid level. Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. Moreover, fugitive emissions in storage systems are mainly from imperfect seals or tank fittings. The amount of emissions from a particular tank will directly depend on the vapour pressure of the product stored. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks [161, USAEPA 1995]. Since that time, emissions from gasoline tanks in Europe have been significantly reduced by the installation of control measures mandated by Directive 94/63 on the control of VOC emissions resulting from the storage of petrol.

VOC emissions from storage can represent more than 40 % of the total VOC emissions in a refinery. The emissions from tanks have been estimated by using API estimations [100, API 2002]. As an example, these emissions can lead to 320 tonnes per year from the storage systems. It is a much lower figure than the one calculated from the DIAL measurements: 1 900 tonnes per year for a refinery processing 11 million tonnes per year [160, Janson 1999]. However, API methods have been updated and storage losses can be predicted with acceptable accuracy [202, Dekkers 2000]. A CONCAWE study [186, Smithers 1995] was the first trial of DIAL where measurements were conducted over a reasonably long period and showed that there was reasonable agreement between DIAL and the latest API estimation methods as to when the test times were long enough. In that case, the estimation method was acceptable to provide annual inventory values. It is important to take into account that the API emissions factor method assumes that no technical problems occur with the considered tank.

DIAL and SOF have now been used for over 20 years, e.g. at Swedish refineries and in France, Belgium, the Netherlands and the US. These monitoring campaigns all give higher results for emissions than calculations. In the beginning, in Sweden, the difference was often close to a factor 10 – 15. Over the years, the factor has become smaller, but a factor 2 – 5 is still common (see also Section 3.26.1.3).

When transferring liquids to vessels at atmospheric pressure, the vapour phase in the receiving vessel, comprising both the vapours existing in the vessel prior to loading and those generated by evaporation of the loaded liquid, is often emitted to atmosphere. Such loading operations are recognised as having an impact on the environment due to the presence of VOCs. VOC emissions from blending come from blending tanks, valves, pumps and mixing operations. The amount depends on design and maintenance of the systems. Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities. One of the largest sources of VOC emissions identified during the Amoco/USAEPA study was fugitive emissions from the loading of tanker barges. It has been estimated that during the loading of products with high partial pressure, 0.05 % of the throughput can be emitted to the air. As previously stated, through the impact of Directive 94/63, air emissions have been significantly reduced in Europe, including those from the barge loading of gasoline.

VOC emissions to the air from cavern storage of hydrocarbon materials can be prevented by connecting the gas spaces of several caverns, so the breathing gases when filling one cavern are led to the other caverns. In the case of only one cavern, the breathing gases must be sent to the

air. For a given product, the VOC emissions from cavern storage are generally slightly lower than from a conventional aerial vessel (of group of vessels) of the same capacity, and the yearly average temperature of storage is lower (5 – 10 °C).

Waste water

Leaking flanges and valves may contaminate rainwater. The amount depends on the maintenance service. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued build up. That waste water is contaminated with tank product. Oil levels of up to 5 g/l in tank water bottoms can be found [159, WB 1998]. However, if the draw-off rate of the water is too high, oil can be entrained with the water, thereby giving a false high reading of oil in the water.

Groundwater leaking into underground storage systems (caverns) should be pumped out and led to the waste water treatment system of the refinery. The amount of water depends on the solidity of the rock and how carefully the fractures in the rock are sealed by injection of concrete [199, Lameranta 2000]. The quality of waste water depends on the product (or crude) which is stored in the cavern. Typically the waste water contains hydrocarbons as emulsion and water-soluble components of stored liquid. Some examples of waste water generated by cavern storage are given in Table 3.82.

Table 3.82: Examples of waste water generated by caverns

| Cavern | Volume of the cavern (m ³) | Product | Seeping water removed (m ³ /yr) | Amount of hydrocarbons discharged after oil separation (kg/yr) |
|--------|--|-------------------|--|--|
| A | 40 000 | Light fuel oil | 22 300 | 49 |
| B | 2x75 000 | Heavy fuel oil | 25 800 | 104 |
| C | 50 000 | Light fuel oil | 36 900 | 40 |
| D | 105 000 | Light condensate | 140 | NA |
| E | 52 000 | Propane/butane | 80 | NA |
| F | 150 000 | Propane/butane | 150 | NA |
| G | 430 000 | Heavy fuel oil | 50 000 | 76 |
| H | 100 000 | Car fuel (diesel) | 5 000 | NA |
| I | 100 000 | Car fuel (petrol) | 3 000 | NA |

Source: [199, Lameranta 2000]

Waste and soil contamination

The primary subsurface (soil and groundwater) contamination threats posed by above-ground storage tanks include the disposal of sludges from the bottoms of the tanks during periodic cleaning of tanks for inspections, loss of product from the tanks during operations such as tank water drainage, and product leakage to the ground caused by tank or piping failures or overfilling accidents. Spills may result in contamination of soil from handling processes, especially in loading, mainly due to human error. Storage tank bottom sludge contains iron rust, clay, sand, water, emulsified oil and wax, phenols and metals (lead for leaded gasoline storage tanks). Table 3.83 shows some analyses of sludges taken from the sewerage system around tank storage facilities. The analyses are unique to that site and are reproduced to show what may occur.

Table 3.83: Composition of the sludge taken from four different sewer systems close to the storage tanks

| Species | Tank field sewers (two different sources) | | Gasoline tank field sewers | Distillate tank field sewers |
|--|--|-----------------------|-------------------------------|---------------------------------|
| | Source 1 | Source 2 | | |
| Solids | 92.7 % | 91.2 % | 81 % | 97.0 % |
| Oil | 7.3 % | 8.8 % | 19 % | 3.0 % |
| Carbon | 26.9 % | 27.1 % | 44.9 % | 58 % |
| Hydrogen | 10.2 % | 15.1 % | 7.8 % | 7.3 % |
| Nitrogen | 1.2 % | <0.6 % ^(*) | 0.4 % | 0.6 % |
| Sulphur | 64441 | 70034 | 58222 | 13514 |
| Iron | 25000.0 | 174024.0 | 62222.0 | 105326.0 |
| Magnesium | 9317.0 | 2695.0 | 4430.0 | 1331.0 |
| Sulphide | 8327.0 | 3624.8 | 4325.9 | 4238.9 |
| Aluminium | 4193.0 | 3969.0 | 8148.0 | 3180.0 |
| Nitrate | 2290.4 | 10.8 | 91.9 | 8.9 |
| Sodium | 1180.0 | 772.0 | 770.0 | 445.0 |
| Sulphate | 1037.3 | 165.5 | 19.3 | 39.7 |
| Xylene | 746.9 | <4.2 ^(*) | 1121.5 | 4.0 |
| Toluene | 478.3 | <4.2 ^(*) | 794.1 | 4.0 |
| Ethylbenzene | 158.4 | <4.2 ^(*) | 106.8 | 4.0 |
| Naphthalene | 130.4 | 27.6 | - | 25.8 |
| Benzene | 80.7 | <4.2 ^(*) | 35.6 | 4.0 |
| Phenol | 71.4 | 129.5 | - | 69.6 |
| Nickel | 68.3 | 106.1 | 500.7 | 190.8 |
| Lead | 55.9 | 492.4 | 308.1 | 234.5 |
| Chromium | 35.4 | 70.5 | 154.1 | 81.5 |
| Pyrene | 30.0 | <105.0 ^(*) | - | 39.0 |
| Carbonate | 29 | 2.0 | 0.3 | 0.3 |
| Vanadium | 27.0 | 72.0 | 49.0 | 25.0 |
| Antimony | 19.0 | 42.0 | 15.0 | 20.0 |
| Phenols | 18.6 | <105.1 ^(*) | - | 39.3 |
| Fluorine | 15.5 | <105.1 ^(*) | - | 39.3 |
| Benzo(a)pyrene | <7.8 ^(**) | <105.1 ^(*) | - | 39.3 |
| Selenium | 7.0 | <4.0 ^(*) | 4.3 | 5.0 |
| Arsenic | 5.0 | 16.1 | 14.5 | 15.9 |
| Mercury | 4.0 | 1.6 | 9.5 | 0.2 |
| Cyanide | 0.6 | 1.0 | 0.5 | 0.7 |
| Calcium | <0.3 ^(*) | 39261.0 | 13185.0 | 11725.0 |
| ^(*) Below detection limit. ^(**) Estimated value below detection limit. NB: Figures quoted on a moisture free basis, all units mg/kg unless otherwise stated. Figures do not sum to 100 % because of double counting. Source: [156, MCG 1991] | | | | |

3.22 Visbreaking and other thermal conversions

3.22.1 Visbreaking

Consumption

Table 3.84 represents the typical utility consumption for a visbreaker.

Table 3.84: Utility consumption of a visbreaker

| Utility (unit) | Consumption range |
|--|-------------------|
| Fuel (MJ/t) | 400 – 800 |
| Electricity (kWh/t) | 10 – 15 |
| Steam consumed (kg/t) | 5 – 30 |
| Cooling water (m ³ /t, $\Delta T=10$ °C) | 2 – 10 |
| NB: The power consumption given is for furnace cracking. Sources: [168, VROM 1999], [204, Canales 2000] | |

For visbreaking, fuel consumption accounts for about 80 % of the operating costs, with a net fuel consumption of 1 – 1.5 % w/w on feed. Fuel requirements for soaker visbreaking are about 30 – 35 % lower.

Emissions

Air emissions

Air emissions from visbreaking include emissions from the combustion of fuels in the process heaters, vents and fugitive emissions. A sour water stream is generated in the fractionator. The gas produced contains H₂S and should be further treated. Hydrogen sulphide and mercaptans are released from the sour water stream from reflux condensers. Hydrocarbons are released from pressure reliefs on reflux drums and vessels, storage and handling operations, spillages and discharges of waste water. Particulate emissions occur during furnace decoking and cleaning operations about twice a year.

Table 3.85 shows the air emissions from visbreaking processes in a European refinery.

Table 3.85: Example of air emissions generated by visbreaking processes

| Installation | Fuel Consumption (GWh/yr) | Throughput (Mt/yr) | Units | SO ₂ | NO _x | CO | CO ₂ | Particulates(*) |
|--|---------------------------|--------------------|-------------------|-----------------|-----------------|-------|-----------------|-----------------|
| TOTAL Refinery Mittel-Deutschland | 306.6 | 1.20 | mg/m ³ | 35 | 100 | 100 | | 5 |
| | | | t/yr | 13 | 50.6 | 1.4 | 59 480 | 0.3 |
| | | | kg/t feed | 0.011 | 0.042 | 0.001 | 50 | 0 |
| Emissions from TOTAL Mitteldeutschland refinery: only limit values are given, loads and specific emissions were calculated. NB: Data are related to yearly average, 3 % O ₂ , dry conditions. (*) No information available on PM size. Source: [191, UBA Austria 1998] | | | | | | | | |

Process waste water

The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate into three phases: a hydrocarbon gas stream, a hydrocarbon liquid stream and a sour water stream. The sour water stream should be sent to the sour water stripper for purification. The flow of waste water generated in the visbreaking process from the sour water drain is around 56 litres per tonne of feedstock. It represents between 1 and 3 % v/v on feed intake.

Table 3.86 shows the range of composition of the visbreaker waste water.

Table 3.86: Typical composition of the waste water produced in visbreaking

| Substance or parameter | Concentration (mg/l) |
|------------------------|----------------------|
| PH | High |
| Free oil | 50 – 100 |
| COD | 500 – 2 000 |
| H ₂ S | 10 – 200 |
| NH ₃ (N-Kj) | 15 – 50 |
| Phenols | 5 – 30 |
| HCN | 10 – 300 |

Solid wastes generated

The waste generated in visbreaking comes from the cleaning and turnaround of the process. It is generated discontinuously at a rate of 20 – 25 tonnes per year for a 5 million tonnes per year refinery. It contains between 0 and 30 % oil/sludge.

The following sections cover the emissions arising from refinery processes that are used for the treatment of waste gas, waste water and solid waste. These techniques are described in Chapter 4 (Sections 4.23 to 4.25). The main objective of these processes is to reduce the concentration of pollutants in the effluents. Obviously the loads and concentrations of pollutants in these streams will be reduced by these processes, but some pollutants will remain in the streams and others may be generated. That is the purpose of the next three sections. Emissions from the refinery as a whole are included in Section 3.1.

3.22.2 Thermal gas oil units (TGU)

Emissions

Table 3.87 shows the emissions to air from one European thermal gas oil unit in OMV Schwechat refinery (Austria).

Table 3.87: Example of emissions of a thermal gas oil unit in a European site

| Installation | Fuel consumption (GWh/yr) | Annual capacity (tonnes/yr) | Units | SO ₂ | NO _x | CO | PM |
|--|---------------------------|-----------------------------|-------------------|-----------------|-----------------|--------|-----|
| TGU OMV Schwechat | 450.1 | 730 000 | mg/m ³ | 0 | 27 – 38 | 2 – 16 | 1 |
| | | | t/yr | <0.1 | 41.7 | 9.3 | 1.3 |
| All data are monthly averages from 2009 at 15 % O ₂ . | | | | | | | |

3.23 Emissions from waste gas treatment techniques

This section includes end-of-pipe or abatement techniques for CO, CO₂, NO_x, particulates, sulphur compounds, VOCs, and combined techniques for the abatement of air pollutants, odour and noise.

3.23.1 Sour gas treatments

The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. The area of the amine treating unit poses health risks because of the presence of H₂S, possibly by inadvertent leakages.

3.23.2 Sulphur recovery units (SRU)

In 1995, the average percentage of sulphur recovered in the SRU represented 42.6 % of the sulphur entering the refinery with the crude oil. From the data gathered for a sample of 50 European sites by the Technical Working Group (TWG) set up for the review of this document, this percentage can be estimated for the period 2007 – 2008 at 44.7 % (50th percentile). However, this median value hides a rather wide range of site performances from 10.7 % to 79.9 % (5th to 95th percentile).

Sulphur is recovered in sulphur recovery units, extensively described in Section 4.23.5. As already shown in Figure 3.12 and Figure 3.13 in Section 3.1.2.4, they represent around 10 – 25 % of the SO₂ emissions from refineries, even if the fuel gas volume from SRU represent only around 1.5 % of the total flue-gas volume emitted by a refinery.

The sulphur recovery yield of SRU operated in a sample of 47 European sites is displayed in Figure 3.36. Values reflect the overall SRU performance, including the utilisation factor achieved by the whole set of available treatment lines. The installed base of SRU has a recovery ranging from 93 % to 99.99 %, with a median value (50th percentile) around 98.5 %.

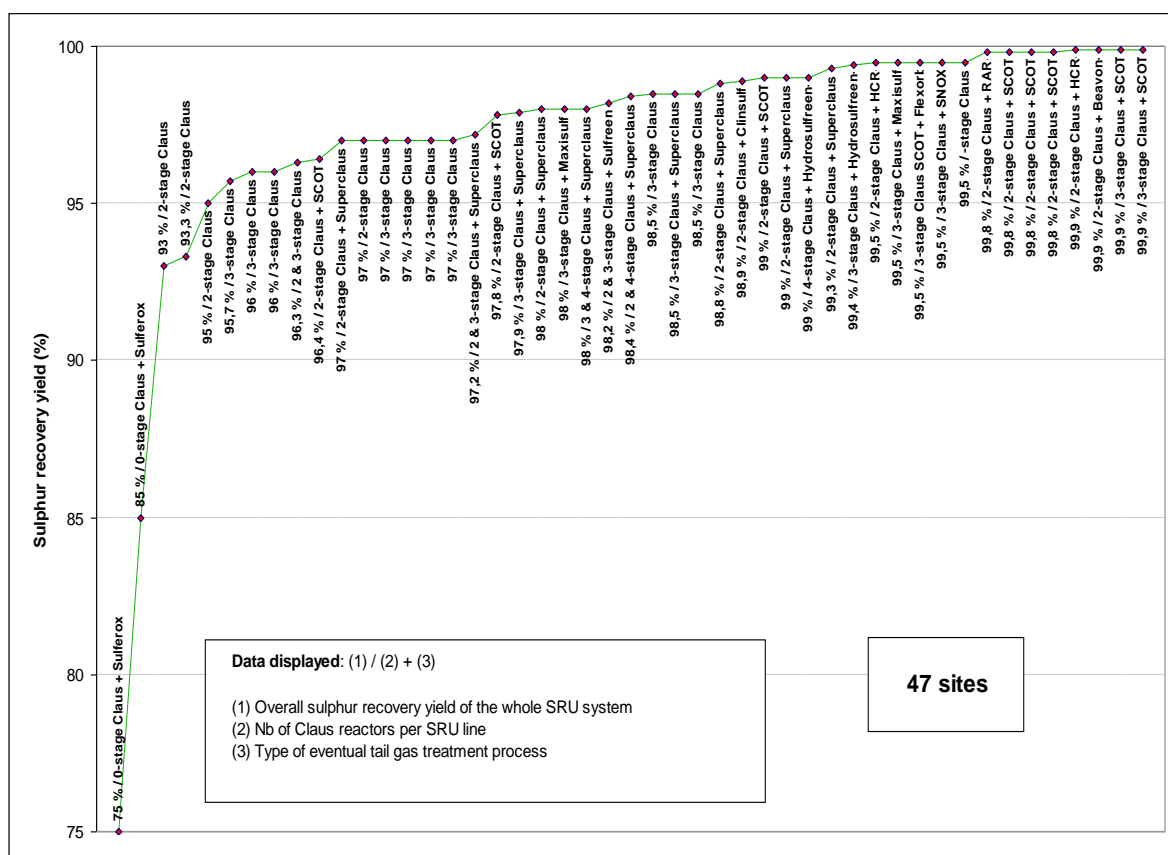


Figure 3.36: Sulphur recovery yield range of SRUs operated in a sample of 47 European sites

From the questionnaire data collection on SRU, SO_2 emissions range from 50 to 52 000 mg/Nm^3 . Emissions from these units typically contain some H_2S , SO_x and NO_x . They also generate process waste water that contains H_2S , NH_3 , amines and Stretford solution. Residual wastes are spent catalysts. The next table shows one example of emissions from European refineries.

Table 3.88: Examples of air emissions generated by sulphur recovery units

| Installation | Fuel consumption (GWh/yr) | Throughput (t/yr) | Units | SO_2 | NO_x | CO | CO_2 | Particulates(*) |
|--|---------------------------|----------------------|------------------------|---------------|---------------|------|---------------|-----------------|
| SRU TOTAL Mittel- Deutschland | 131.4 | 90 000 of sulphur | mg/m^3 | 4 322 | 200 | 100 | | 50 |
| | | | t/yr | 1 125.6 | 52.1 | 26.0 | 25 492 | 13 |
| | | | kg/t feed | 12.5 | 0.58 | 0.29 | 283.2 | 0.15 |

NB: Data are related to yearly average, 3 % O_2 , dry conditions.
 For the Mitteldeutschland refinery, only limit values are given.
 Loads and specific emissions were calculated.
 (*) No information available on PM size.

3.23.3 Flares

Flaring is both a source of air emissions and has the potential to burn valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. It is generally restricted to unplanned shutdowns or emergency cases. More information is available in the CWW BREF [6, COM 2003].

Consumption

The main utilities that flare systems will use are refinery fuel gas or nitrogen for purging the flare headers, fuel gas for the pilot burners and steam for heating purposes. However, the consumption of these utilities is very low under normal operating conditions.

Emissions

Flaring activity varies according to the real-time opportunity for refinery management optimisation. It may lead to extreme values during incidents, shutdowns or major maintenance periods. As an example, the following gives the evolution of the annual flare output for a German refinery which faced a major maintenance period for the installation of a new technique in 2007, as compared with the seven previous years.

Table 3.89: Evolution of the flaring activity according to annual maintenance programme

| | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | 2007 |
|----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Crude input (Mt/yr) | 3.08 | 3.42 | 3.40 | 3.43 | 3.53 | 3.41 | 3.35 | 2.53 |
| Flare output (t/yr) | 704 | 201 | 560 | 1 003 | 390 | 753 | 165 | 6 155 |
| Flaring ratio (‰) | 0.23 | 0.06 | 0.16 | 0.29 | 0.11 | 0.22 | 0.05 | 2.43 |

Source: [28, Tebert et al.2009]

Another example, from two refineries in Sweden, gives the following flaring ratios.

Table 3.90: Example of flaring ratio of two refineries in Sweden

| | Flaring ratio (‰) | |
|----------------------------------|-------------------|------------|
| | 2008 | 2009 |
| Preem Gothenburg refinery | 0.6 | 0.6 |
| Preem Lysekil refinery | 0.8 | 1.0 |

Flares emit at least CO, CO₂, SO₂ and NO_x. Under specific conditions, flaring leads to soot formation and VOC emissions. Small amounts of complex hydrocarbons (e.g. PAH), may also be released. Based on [86, SFT 2009], there is a clear link between soot formation and small emissions of PAH compared to other sources. Emissions of dioxins from flaring were considered as non-existent, mainly due to the absence of necessary formation conditions. Conditions for emissions of PCB were regarded as highly unlikely.

The composition depends on a number of factors, including the composition of flare gas, flaring rate, flare system, wind and combustion efficiency at the flare tip. Flares are a very important point source of refinery emissions. Some plants still use older, less efficient waste gas flares. Because these flares usually burn at temperatures lower than necessary for complete combustion (minimum 850 °C), larger emissions of hydrocarbons and particulate, as well as H₂S, can occur. Noise from a flare has two components: flow noise and combustion noise. Flow noise occurs when the flare gas is flowing out of the flare tip at high speed. The greater the amount of flare gas, the more noise. Combustion noise is generated in the combustion zone. A short intense flame, where the energy turnover is fast and in low volume, generates more noise than if this occurs in a larger volume.

3.24 Emissions from waste water treatment techniques

Large volumes of waste water are released by the petroleum refining industry. Waste water treatment plants are advanced environmental protection systems for the control of surface water pollution. However, as this treatment is not complete the resulting discharges still contain pollutants that can contaminate the receiving environment. Moreover, during treatment a portion of the pollutants evaporate, leading to aerial emissions that may be significant depending on the type of treatment applied. The contributors to the influent of the treatment process are the desalters, storage tank drainage systems, slop system and other processes that have direct water-product contacts.

Process effluent volume can be compared to the volumes of process effluent discharged (excluding once-through cooling water). Although related, the values are not identical given that there are other sources of water to the effluent system including rainwater on plant surfaces, water separated from crude, ballast water, etc. Moreover, some water will be consumed by evaporation, be used in chemical reactions, etc. As a general trend, refineries are progressively treating less crude or throughput compared to their capacity because of more complex refining schemes, products specifications, and choices (e.g. more gas oil and less gasoline). Thus, the effluent volume per tonne of throughput also depends on the operations performed at the refinery.

Table 3.91 displays the data on water discharge volumes that have been made available to the TWG for 41 European refineries with dedicated waste water treatment plants. Data displayed here are drawn from released waste water while those in Table 3.3 are from consumption water.

Table 3.91: Summary data on the volume of waste water from 41 European refineries

| Type of waste water | Volume discharged | Unit | Range (5th–95th percentiles) | Median (50th percentile) |
|---|-------------------|----------------------------|------------------------------|--------------------------|
| Waste water from process ^(*) | Annual | million m ³ /yr | 0.55 – 10 | 2.58 |
| | Specific | m ³ /t | 0.11 – 1.57 | 0.38 |
| Waste water from cooling | Annual | million m ³ /yr | 0 – 212 | 0.9 |
| | Specific | m ³ /t | 0 – 58 | 0.08 |
| Potentially contaminated rainwater | Annual | million m ³ /yr | 0.09 – 2.3 | 0.48 |
| | Specific | m ³ /t | 0.02 – 0.2 | 0.08 |
| Total waste water | Annual | million m ³ /yr | 0.54 – 65 | 2.9 |
| | Specific | m ³ /t | 0.15 – 11.68 | 0.44 |
| ^(*) Waste water from process: Waste water annual release reported as from process. Sources: [TWG site questionnaires]; annual averages reported for 2006, 2007 or 2008 - Dedicated WWTP | | | | |

Emissions

Air emissions

- The air emissions from waste water treatment plants stem from evaporation (hydrocarbons, benzene, H₂S, NH₃, mercaptans) from the numerous tanks, ponds and sewerage system drains that expose their surfaces to air. The sewage system and the waste water treatment in a refinery may be sources of odour nuisance, particularly from open drains and from oil separators. VOCs are also emitted during air stripping in flotation units and in the biotreater. The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [167, VDI 2000]:
- 20 g/m² per hour for open oil separator;
- 2 g/m² per hour for covered oil separator;
- 2 g/m² per hour for flotation;
- 0.2 g/m² per hour for biological treatments.

Other methods to calculate emissions are available such as the Litchfield correlation. [275, Litchfield 1971].

Emissions to water

Potential releases into water consist of the residual substances contained in the effluent after treatment. Depending on the nature of the refinery and the treatment efficiency, these may include carbon compounds (insoluble and soluble), nitrogen compounds (organic and inorganic; oxidised and reduced), sulphur compounds (oxidised and reduced), and metals and their compounds. More information on effluent composition downstream of a waste water treatment based on a questionnaire data collection (2008) is included in Section 3.1.3.

Solid wastes generated

The limited information reported in the survey (for three units [166, CONCAWE 1999]) indicated an annual sludge production of about 2 400 tonnes per year for a throughput of 600 m³/h. The induced air flotation generates 600 tonnes per year with a unit operating at 600 m³/h.

Refinery waste water collection and pretreatment systems generate important amounts of solid wastes that have been in direct contact with hydrocarbons:

- Settleable solids (specific gravity greater than water) can separate from waste water in the collection and primary treatment systems. The collection system can include individual drain systems serving production areas as well as other areas affected by refinery activities and may include basins and/or tank systems to contain and manage peak flows of storm water.
- Suspended solids (specific gravity less than or equal to water) may be separated and extracted in gas flotation or sand filtration processes. Secondary biological treatment processes can generate important amounts of excess biosolid waste that must be continually removed from the process, as soluble substances are assimilated into new biomass in the bioreactors.

Table 3.92 shows the composition of the different sludges generated in the waste water treatment plants.

Table 3.92: Examples of analysis of refinery sludges

| Species | API separator | Activated sludge | Settling basin plant |
|--|----------------------|------------------|----------------------|
| Solids | 90.4 % | 94.3 % | 99.7 % |
| Oil | 9.6 % | 5.7 % | 0.3 % |
| Carbon | 25.8 % | 13.1 % | 1.7 % |
| Hydrogen | 13.1 % | 51.8 % | 6.3 % |
| Nitrogen | 0.6 % ^(*) | 1.7 % | 0.5 % |
| Sulphur | 40733 | 9479.0 | 4214.0 |
| Carbonate | 0.3 % | 0.2 % | 0.1 % |
| Iron | 48269.0 | 10900.0 | 7131.0 |
| Aluminium | 43177.0 | 2322.0 | 4878.0 |
| Calcium | 11609.0 | 4692.0 | 8104.0 |
| Sulphide | 6180.2 | 2165.9 | 103.7 |
| Magnesium | 4878.0 | 1351.0 | 1767.0 |
| Sodium | 1711.0 | 3981.0 | 3971.0 |
| Xylene | 469.5 | 9.5 | 3.2 |
| Naphthalene | 288.2 | 46.9 | 16.0 |
| Lead | 279.0 | 49.3 | 15.2 |
| Phenol | 265.0 | 46.9 | 16.0 |
| Nickel | 252.5 | 37.9 | 8.8 |
| Nitrate | 228.1 | 2066.4 | 194.5 |
| Toluene | 138.5 | 9.5 | 32 |
| Styrene | 134.4 | 47 | 16.0 |
| Vanadium | 99.0 | 18.0 | 24.0 |
| Ethylbenzene | 82.5 | 9.5 | 3.2 |
| Chromium | 80.0 | 8.1 | 11.2 |
| Fluorine | 59.1 | 46.9 | 16.0 |
| Antimony | 49.0 | 14.0 | 5.0 |
| Benzo(a)pyrene | 42.6 | 46.9 | 16.0 |
| Phenol | 40.3 | 46.9 | 16.0 |
| Selenium | 35.4 | 26.0 | 9.0 |
| Benzene | 13.2 | 9.5 | 3.2 |
| Sulphate | 12.2 | 2767.8 | 285.3 |
| Arsenic | 6.5 | 15.2 | 5.2 |
| Mercury | 3.0 | 1.0 | 0.0 |
| Cyanide | 1.0 | 7.0 | 0.7 |
| ^(*) Below detection limit. NB: Figures do not sum to 100 % because of double counting. Figures quoted on a moisture-free basis, all units mg/kg unless otherwise stated. Source: [156, MCG 1991] | | | |

3.25 Waste generation

An important issue when considering refinery waste is that there are still many differing definitions between countries, which makes comparisons of waste difficult.

Sludges

The amount of sludge generated depends on the types of processes and the availability of incineration. As a common figure, the generation rate of solid waste and sludges is normally less than 0.5 % of crude processed, but in some refineries it is less than 0.3 %. Annual sludge generation was 1 250 kt per year (in 1993), some 0.2 % of refinery intake.

In 1993, CONCAWE carried out a survey of waste in western European refineries [157, CONCAWE 1995]. In this survey 89 refineries reported their sludge production from all sources as one million tonnes. That means an average of 11 000 tonnes per year per refinery. This figure represents 0.20 % of the crude oil processed by these refineries. However, a variation range from 2.5 % to less than 0.02 % was found in European refineries, with the value being independent of the type of refinery. From that million tonnes of waste, 45 % was sludge, 20 % other refining wastes and the rest non-refining wastes. Sludges come from stabilisation processes (4.7 % of the total sludge generated after treatments), waste water sludges (39.8 %) and sludges with no treatment (55.5 %).

The total amount of identified other refining wastes which are specific to the refining process (e.g. spent catalysts, tank scales, contaminated soils) produced in 1993 by the 89 European refineries reporting was 201 983 tonnes (i.e. 0.04 % w/w of the total refinery throughput). Data provided by 16 EU+ refineries show that the specific production of waste ranges from 133 to 4 200 t/million t of crude. Table 3.93 shows the waste routes statistics for 2007 and 2009 in refineries.

Table 3.93: Waste routes and transfers in the refinery sector in 2007 and 2009

| Type of waste and transfer | Routes | 2007 | | 2009 | |
|-------------------------------------|-----------------|----------------|-----------------|----------------|-----------------|
| | | Tonnes | Number of sites | Tonnes | Number of sites |
| Hazardous waste in the country | Disposal | 294 000 | 103 | 405 000 | 105 |
| | Recovery | 306 000 | 98 | 372 000 | 103 |
| Hazardous waste outside the country | Disposal | 3 000 | 5 | 4 000 | 3 |
| | Recovery | 34 000 | 30 | 19 000 | 23 |
| Total hazardous waste | | 637 000 | - | 800 000 | - |
| Non-hazardous waste | Disposal | 372 000 | 60 | 262 000 | 59 |
| | Recovery | 538 000 | 61 | 500 000 | 64 |
| Total non-hazardous waste | | 900 000 | - | 762 000 | - |

Sources: E-PRTR and CONCAWE

Spent catalyst

Hydroprocessing requires the use of catalysts to remove impurities and to convert the oil into more useful products. The catalysts used consist mainly of oxides of nickel, cobalt and molybdenum on an alumina carrier. During hydroprocessing operations, the catalysts are loaded with sulphur, vanadium and coke. The porosity of the catalysts decreases and their activity is reduced, which eventually requires replacement of the catalyst in the reactors. Consequently, the catalysts become spent and must be replaced.

Co/Mo catalysts are used in hydrodesulphurisation, hydrocracking and hydrotreating. A 5 Mt/yr refinery typically generates from 50 to 200 t/yr spent Co/Mo catalyst.

Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. A 5 Mt/yr refinery typically generates 20 – 100 t/yr spent Ni/Mo catalyst.

Ni/W catalysts are used in lube oil hydrofinishing. There are limitations for disposal in view of the high tungsten content (24 % w/w). A 50 000 t/yr lube oil plant can generate 50 t/yr of this catalyst waste.

FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries (world production is about 0.5 Mt/yr). A 1 Mt/yr FCC unit generates 400 – 500 t/yr, predominantly as FCC fines if an ESP is installed. For a RCC, this amount can be a factor of 5 – 10 higher, depending on the type of feed, as spent catalyst is withdrawn from the regenerator.

Reformer and isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved. Typical average amounts involve 20 – 25 t/yr for a 5 Mt/yr refinery. If necessary, guard beds of HDS catalysts are used for protection and extension of the lifetime of the expensive catalysts.

Hydrodemetallisation catalysts typically have high vanadium contents (10 – 20 %) and are currently alumina based (used to be silica). The annual amount for regeneration is in the order of 500 – 1 000 t/yr for Hycon (Shell Pernis NL), dependent on the feed quality.

Zn-containing beds from H₂ plants are typically recycled to the zinc industry where ZnS ores are processed. Amounts are some 50 t/yr.

In hydrodesulphurisation, hydrotreating and hydrocracking, the world catalyst production (and thus also the generation of spent catalysts) grew considerably during the 1990s and was estimated at 100 kt/yr (1998). At the same time, regeneration capacity was estimated at 125 kt/yr. It was also estimated that 5 – 10 % of this category of spent catalysts was still being landfilled.

Table 3.94: Composition of spent catalysts from various sources in % w/w

| Process | S | C | Mo | V | Ni | Co | Al | Other |
|-----------------------------|--------|---------|-------|-------------------------|-------------------------|-------|---------|----------------|
| FCC, RCC | <1 | <1 | | 4 – 8000 ^(*) | 2 – 3000 ^(*) | | 30 | |
| Reforming and isomerisation | | | | | | | 30 | 0.5 Pt, Pa, Rh |
| Hydro-processing | 6 – 16 | 10 – 30 | 4 – 8 | 2 – 12 | 1 – 2 | 1 – 2 | 20 – 30 | |
| Claus plant | 5 | 5 | 4 – 8 | | 2 – 3 | | 20 – 30 | |
| Hydrofinishing | 5 | 1 – 2 | | | 2 – 4 | | 30 | 24 W |
| Hydrogenation | 5 – 15 | | | | | | 0 | 30 Zn |
| Hydro-demetallisation | 5 – 15 | 10 – 30 | | 10 – 20 | 2 – 5 | | 30 | |

(*) In ppm

3.26 Monitoring

There is a specific document [46, COM 2003] on monitoring (MON) and an expanding series of literature published by competent authorities at federal and national levels (e.g. HMIP Technical Guidance Notes in the UK). These documents contain information on theory, methodology and related techniques. It should be considered that the requirements and frequency of sampling, analysis and type of monitoring requirements are site- and/or process-specific. They are influenced by consideration of the anticipated volume and composition of the waste streams and are included in the permits. The MON document also provides guidance to permit writers on compliance assessment and environmental reporting, and encourages the comparability and reliability of monitoring data across Europe. To enable the comparability of data monitored in Europe, attention should be paid to different monitoring standards and the reference conditions used for example. Details on detection limits of current monitoring methods, e.g. for emissions to water, are available in the MON document.

This section aims to give recommendations on the scope and frequency (continuously or discontinuously) of monitoring streams in a refinery. Monitoring should be undertaken during commissioning, start-up, normal operation, and shutdown unless it is agreed that it would be inappropriate to do so.

The monitoring system should allow adequate processing and emission control. A monitoring system in a refinery generally includes:

- continuous monitoring of pollutants for high volume flows with high variability in pollutant concentrations;
- periodic monitoring or the use of emission relevant parameters for flows with a low variability and calculation based on high-quality emission factors;
- regular calibrating of measurement equipment;
- periodic verification of measurement by simultaneous comparative measurements.

In order to have a good idea of the emissions generated by an installation (e.g. a refinery), the emissions need to be quantified. This will give the refinery and permit writer the ability to know where the actions to reduce a certain pollutant may be more economical. Typically abating higher emissions at high concentrations is more economical than lower emissions at low concentrations. As a consequence, a quantification of the emissions for each single refinery is the first starting point in any environmental assessment. This quantification may contain a full mass balance also considering other outputs (e.g. products).

3.26.1 Monitoring of emissions to air

SO₂, NO_x, particulate matter and CO are typically continuously monitored (on-line or predictive) in the refineries. Records of the volumes are also required for the calculation of the load (tonnes of pollutant per year) or for the application of the bubble concept. Table 3.95 shows the locations where the main air pollutants are typically monitored in a refinery.

Table 3.95: Examples of the most common air emission monitoring in oil refineries

| Parameter | Example of monitoring | Location where normally is measured |
|--------------------|--|---|
| Sulphur dioxide | Continuous if P>30 MW (except for natural gas) Continuous if P >20 MW and desulphurisation unit (elsewhere, daily estimation) or P >100 MW | FCC unit regenerators Sulphur recovery units (i.e. from tail gas incinerators) Incinerators or furnaces used to burn sour gas or liquid fuels Bitumen production units Gasification units Coking processes |
| Oxides of nitrogen | Continuous if >30 MW (except for natural gas) Continuous if P>20 MW and abatement unit or P >100 MW | Combustion processes FCC unit regenerators Gasification units Coking processes |
| Carbon monoxide | Continuous if P >10 MW Continuous if P >50 MW | FCC unit regenerators (for partial combustion type units if CO release is significant). Combustion processes |
| Particulate matter | Continuous for solid and liquid fuels if >10 MW Not relevant for natural gas or RFG (Examples from Austria) Continuous if P >50 MW (Examples from France – P expressed as MW th) | Combustion processes burning fuel oil FCC unit regenerators Coking processes and petroleum coke calciners and coolers Gasification units Catalyst regeneration (e.g. reforming) |

Other common emission components to air commonly monitored are:

- carbon dioxide
- nitrous oxide
- volatile organic compounds (VOCs)
- heavy metals
- hydrogen fluoride
- halide compounds
- ammonia (NH₃)
- hydrocarbons (as unburnt hydrocarbons, UHC)
- dioxins and/or POPs.

The following sections include monitoring practices that have been found in European refineries.

3.26.1.1 Sulphur monitoring

It can be expected that the operators compute site sulphur balances over appropriate time periods as a part of monitoring their operations. The time period may vary according to the circumstances (e.g. how often feedstocks change) but could typically be quarterly. In the case of SO_x, the amount emitted by combustion processes may be calculated from the analysis of the fuel being burnt. In some countries (e.g. France), a sulphur balance is established daily by the operator and sent monthly to the competent authorities.

3.26.1.2 Emissions from combustion processes

The monitoring of emissions is carried out to determine the concentration of regulated substances in the flue-gas under standard conditions so that they can be reported, or to control

the combustion process or abatement plant. Gaseous releases from gas turbines used for electrical generation or gas compression are typically also monitored.

In order to relate emission concentrations to mass releases, it will be necessary to determine the gas flow by direct measurement or other means. Additionally, in order to relate measurements to reference conditions, the temperature will need to be determined. The determination of oxygen and water vapour content may also be required. Monitoring and averaging periods required by the type of substances and the techniques used also need to be reported.

3.26.1.3 Diffuse VOC monitoring

Diffuse VOC emissions are emissions arising from direct contact of gaseous or liquid volatile organic compounds with the environment (atmosphere, under normal operating circumstances). These can result from:

- inherent design of the equipment (e.g. uncovered oil/water separators);
- operating conditions (e.g. non-collected vent of a fixed roof tank during loading);
- or fugitive emissions caused by an undesired gradual loss of tightness from a piece of equipment and a resulting leak. Fugitive emissions are a subset of diffuse emissions.

VOC emissions from refineries come mainly from diffuse emissions. Four major diffuse emissions sources can be identified.

- Fugitive emissions from leaking equipment in the process area, such as valves, flanges, pumps, safety valves, etc. They usually account for 20 – 50 % of the total refinery VOC emission. Emissions may also be high after start-up operations due for example to a poorly undertaken tightening of equipment.
- Crude oil and products storage. External and internal floating roof tanks are emission sources because of evaporative losses that occur during standing storage and withdrawal of liquid from the tank. Emissions from fixed roof tanks are due to the venting during operations or to breathing due to variation of ambient temperature. Emissions from floating roof tanks occur from losses from seals and roof fittings. They typically represent 20 – 40 % of the refinery emissions.
- Loading and unloading facilities, including road tankers, rail tank cars, barges and sea-going vessels. They account for 5 – 10 % of site emissions.
- Waste water treatment plants, where a gradual release of VOCs may occur at all water/air interfaces. Depending on VOC-reducing techniques applied, WWTPs usually generate 5 – 30 % of the total site emissions.

Overview of available methods for detection/quantification

The main available methods with their respective field and scale of application are displayed in Table 3.96. It can be remarked that all these methods are complementary and all potentially useful in order to build up an efficient monitoring programme. Some are appropriate for the detection and/or the quantification of spot sources, whereas others are devoted to area sources, and unit-scale or even site-scale global emissions. Moreover, each of these methods enables the monitoring of a different scope of VOC species, as seen in Table 3.97.

On one hand, it has to be emphasised that calculation methods based on emission factors and algorithms are reported to be unreliable and give significantly underestimated results, in particular for tank farms, cokers and flares [50, White.2008], [51, Chambers et al.2006].

On the other hand, a CONCAWE report [62, CONCAWE 2008] highlighted the potential errors introduced by using short-term values for extrapolation to annual ones due to the temporal variations in the emissions from diffuse sources. Some estimation algorithms (e.g. for storage) have been derived from extensive tests and are designed specifically to provide long-term estimates. However, these calculation methods represent an average situation and do not

take into account unexpected emissions causes (e.g. defective seals, contaminated cooling water). In addition, refineries need to perform measurements to obtain information on these unknown emission sources.

Table 3.96: Overview of main available methods for VOC detection and quantification

| Type of diffuse VOC source | Calculations | | Measurements | | | | |
|---|------------------------------------|--|---|---------------------------|------------------------------|--|--------------|
| | Emission factors and/or algorithms | Specific modelling (e.g. US TANKS, WATERS 9 codes, ToxChem+) | 'Sniffing' and correlation curves (EN 15446:2008) | Optical gas imaging (OGI) | Solar Occultation Flux (SOF) | Differential absorption (LIDAR – DIAL) | Flux chamber |
| Small individual equipment (pumps, valves, flanges, etc.) | Q | | D/Q | D ⁽¹⁾ | | | |
| Storage tanks | Q ⁽³⁾ | Q | | D ⁽¹⁾ | D/Q ⁽²⁾ | D/Q ⁽²⁾ | |
| Loading/unloading facilities | Q | | | D ⁽¹⁾ | D/Q | D/Q | |
| Water treatment plants | Q | Q | | | D/Q ⁽²⁾ | D/Q ⁽²⁾ | Q |
| Full scale unit/Whole site | Q ⁽⁴⁾ | | | | D/Q | D/Q | |

NB: **D** = detection **Q** = quantification
⁽¹⁾ The detection exhaustiveness regarding mass flow rate has to be confirmed.
⁽²⁾ Active area sources can be detected if they generate individual plumes that can be distinguished from the rest of the site, and if emissions occur during the measurement.
⁽³⁾ Algorithms designed for annual emission quantification.
⁽⁴⁾ Emission factors and algorithms cannot estimate the complete set of possible emissions sources and operating conditions (e.g. heat exchangers, defective floating roof seals, inaccessible leaking equipment).

Table 3.97: Overview of VOC species according to the measuring method applied

| VOC species | Measurements | | | | |
|---------------------|---|---------------------------|------------------------------|--|------------------|
| | 'Sniffing' and correlation curves (EN 15446:2008) | Optical gas imaging (OGI) | Solar Occultation Flux (SOF) | Differential absorption (LIDAR – DIAL) | Flux chamber |
| Alkanes | Y | Y | Y | Y ⁽¹⁾ | Y ⁽⁴⁾ |
| Alkenes | Y | Y | Y | Y ⁽¹⁾ | Y ⁽⁴⁾ |
| Aromatics | Y | Poor ⁽³⁾ | N | Y ⁽²⁾ | Y ⁽⁴⁾ |
| Cyclic hydrocarbons | Y | Y | Y | Y ⁽¹⁾ | Y ⁽⁴⁾ |
| Methane | Y | Y | N | Y ⁽¹⁾ | Y ⁽⁴⁾ |
| Total VOC | Y | Y | Y | Y | Y |

⁽¹⁾ When based on IR light.
⁽²⁾ When based on UV light.
⁽³⁾ Poor for light aromatics when based on passive systems (2009 data).
⁽⁴⁾ With GC/MS used for speciating samples.

Description, main features and limitations of most used measuring techniques

This section gives a short description of the four monitoring techniques based on actual measuring which are most commonly used for the monitoring of diffuse VOC emissions. Respective costs, detection limits together with a comparison of their specific advantages and drawbacks are summarised in Table 3.99. Calculation methods cannot be considered measurements and will not be described in this section.

Method EN 15446:2008: conventional VOC ‘sniffing’

This method was originally developed as a support for the implementation of a LDAR programme (see Section 4.23.6.1) for the detection and ranking of leaking equipment pieces to be repaired. The first step is the detection (‘sniffing’) which is achieved using hand-held VOC analysers measuring the atmospheric VOC concentration adjacent to the equipment, as shown in Figure 3.37. The most frequently used measuring techniques are the flame ionisation (FID) and the photo-ionisation (PID), calibrated to operate in the range of 10 – 100 000 ppmv. The probe is characterised by a ‘response factor’ which takes into account the sensitivity to the actual VOC mixture measured compared to a reference gas, and a ‘response time’ defined as the time needed to register 90 % of a concentration step change. Both factors greatly influence the results and have to be optimised according to the EN 15446 standards.



Figure 3.37: Leak concentration measurement



Figure 3.38: Bagging of a leaking valve

For mass flow quantification, the second step proposed by the standard method consists of bagging the source component as shown in Figure 3.38. This bagging is the only step of this method allowing for a direct measurement at the source of emission. However, as bagging is an extremely burdensome operation and is not always possible, mathematical correlation curves can be derived from statistical results obtained from a sufficiently large number of previous measurements of both leak concentration (Step 1) and mass flow (Step 2) made on similar components. Very few refineries have developed such correlation curves corresponding to their own set of components, related VOC leakage mixtures, and concentration measurement skills and real practices. Alternatively they use generic curves from the literature based on extensive measurement campaigns carried out on US facilities in the 1950s – 1980s and 1990s.

Optical gas imaging techniques (OGI)

Optical imaging uses small lightweight hand-held cameras which enable the visualisation of gas leaks in real time, so that they appear as ‘smoke’ on a video recorder together with the normal image of the component concerned. This technique is primarily used to easily and rapidly locate significant VOC leaks, e.g. on process components, storage tanks fittings, pipeline flanges or vents. Most current commercial OGI cameras fall under one of these two categories.

- *Active systems* where the image is produced by a back-scattered IR laser light reflected on the component and its surroundings. The laser wavelength is optimised to be absorbed by the VOC concerned.
- *Passive systems* based on the natural IR radiation of the equipment and its surroundings. The contrast of the VOC image is based on the plume IR absorption and the heat radiance difference between the plume and its background. An optical filter selects the optimal IR wavelength according to the VOC nature.

Detection limits are related to the minimal thermal gradient for visualisation, and will depend on the gas temperature, the distance from the source, and the wind speed. Although these are higher than achieved by ‘sniffing’, OGI technology can more efficiently identify the main fugitive

emission sources. The mass emission rate is still not directly quantified. Specific work is being done in order to propose and validate appropriate OGI emission factors based on comparison with EN 15446 quantification on the same set of components in an actual unit. In addition, the US API also developed OGI leak/no-leak factors.



Figure 3.39: An OGI video camera

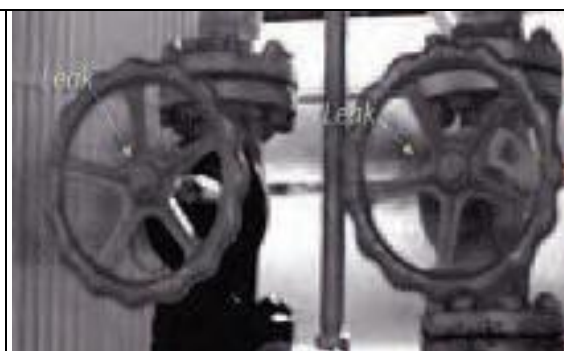


Figure 3.40: Typical visualisation of gas leak

Differential absorption lidar (DIAL)

DIAL is a laser-based technique using differential absorption LIDAR (light detection and ranging) which is the optical analogue of radio wave-based RADAR. As shown in Figure 3.41, the technique relies on the back-scattering of laser beam pulses by atmospheric aerosols, and the analysis of spectral properties of the returned light collected with a telescope. As each molecule present will absorb and re-emit a typical light, the returned beam acts as an optical signature of the concentration of most molecules present between the DIAL source and the reflecting particulate. By sampling the returned light pulse rapidly according to time, it is possible to distinguish how far each sample of the light pulse has travelled and, thus, locate it with the precision of a few metres in optimum conditions.

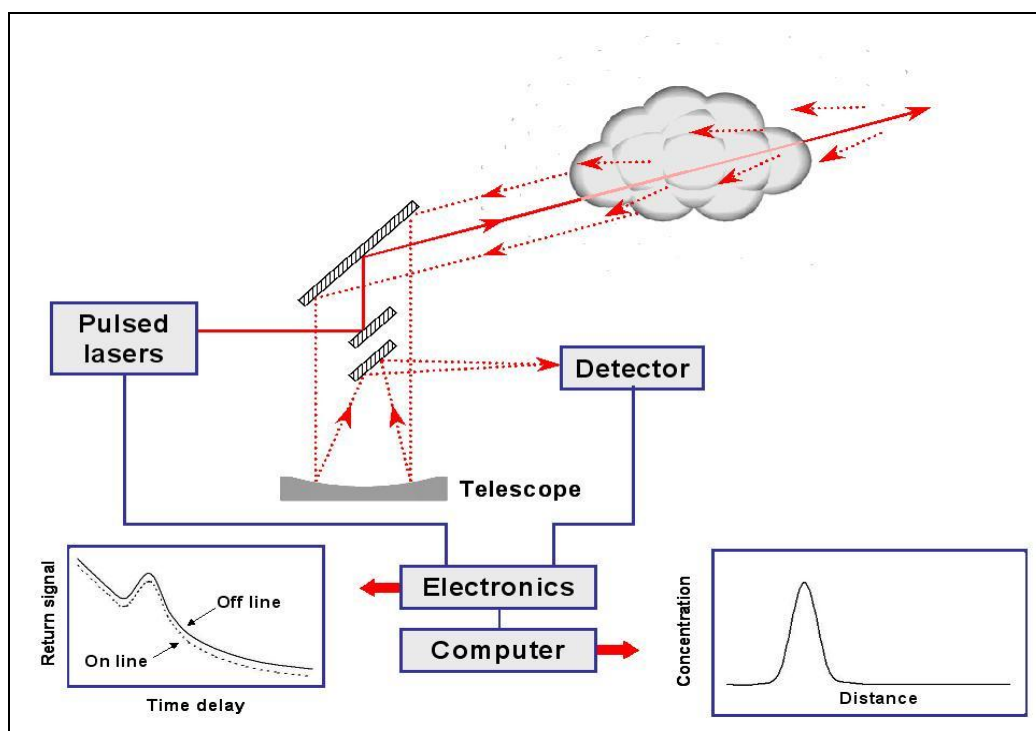
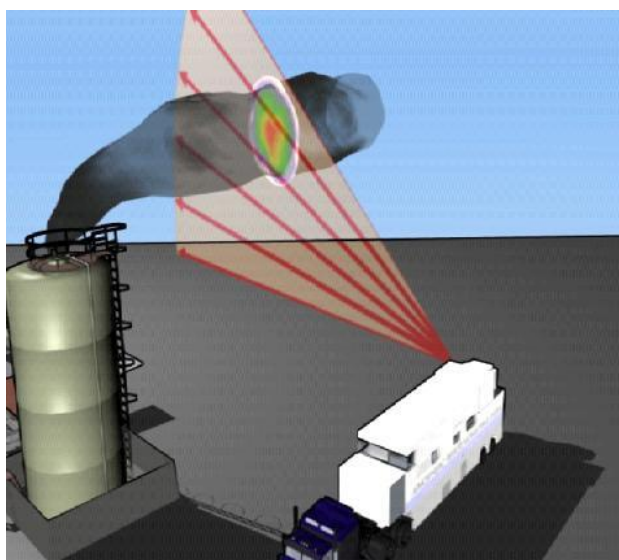


Figure 3.41: Scheme of the DIAL process



The laser beam and the optical reception system are rotated in order to cover a plane crossing the atmospheric VOC plume. The result of it is a two-dimensional map where the concentration can be integrated, as shown in Figure 3.42.

To obtain mass emission flux, the concentration data across the plume section should be multiplied by the wind velocity reported perpendicularly to the measurement plane.

Wind data availability, accuracy and representativeness are essential for reducing quantification uncertainties.

Typical sensitivities and maximum distance ranges are given in Table 3.98 for various emitted VOCs and other compounds of interest. Sensitivities apply at a range of 200 m for a 50 m wide plume.

Table 3.98: DIAL sensitivity and maximal distance range for various emitted compounds

| Infrared DIAL system | | | UV/Visible DIAL system | | |
|----------------------|-------------------|------------|------------------------|-------------------|------------|
| Species | Sensitivity (ppb) | Max. range | Species | Sensitivity (ppb) | Max. range |
| Methane | 50 | 1 km | Benzene | 10 | 800 m |
| Acetylene | 40 | 800 m | Toluene | 10 | 800 m |
| Ethylene | 10 | 800 m | Xylenes | 20 | 500 m |
| Ethane | 20 | 800 m | NO | 5 | 500 m |
| Higher alkanes | 40 | 800 m | NO ₂ | 10 | 500 m |
| HCl | 20 | 1 km | SO ₂ | 10 | 3 km |
| N ₂ O | 100 | 800 m | Ozone | 5 | 2 km |
| Methanol | 200 | 500 m | Mercury | 0.5 | 3 km |

Various field validation measurements were performed and gave the following results:

- Repeated DIAL measurements downwind of a calibrated (10 kg/h) source of methane agreed to within +/- 10 % of emitted value;
- Comparison with a line of pumped absorption tube samplers inside a chemical plant agreed with DIAL measurements of aliphatic hydrocarbons to within +/- 12 %, and toluene to within +/- 15 %;
- VOC emission measurements from a petrochemical storage facility made by DIAL and standard point sampling methods agreed to within +/- 8 %;
- SO₂ plume from a tail gas incinerator (340 kg/h) agreed to within -11 %;
- NO plume from a gas turbine power plant (66 kg/h) agreed to within +1 %.

However, the overall uncertainty in industrial field conditions is evaluated at around 30 – 50 %, most of it from wind speed evaluation. A reduction of this uncertainty may be possible by making wind measurements at various heights in, or close to, the DIAL scan plane. As with all short-term measurement techniques, the extrapolation to provide values of annual emissions for inventory purposes introduces further potential for error, particularly as the majority of refinery VOC sources have significant emission variations with time.

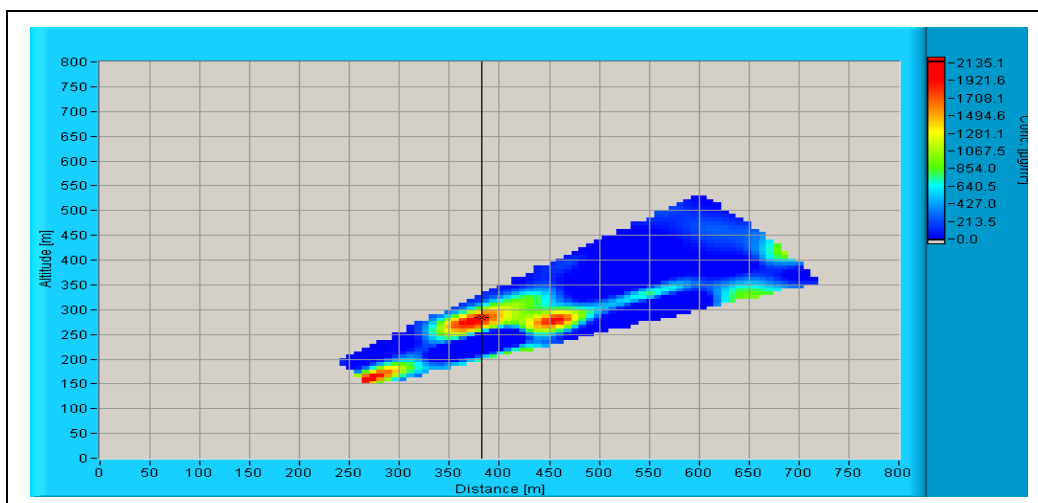
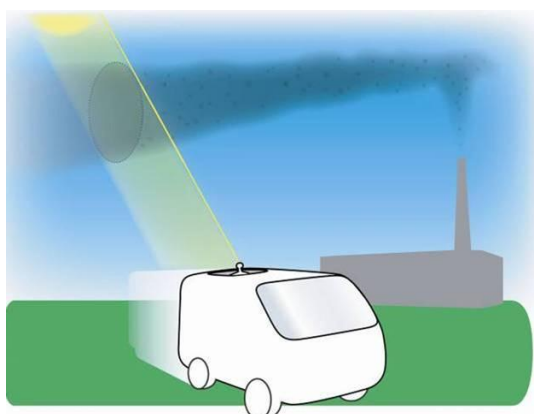


Figure 3.42: Typical DIAL concentration map obtained with DIAL measuring system

Solar Occultation Flux (SOF)

The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband IR or UV/Visible sunlight spectra along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes



The system is permanently guided to the sun by a solar tracker mirror, which reflects the sunlight into the spectrometer independent of its position. On short distance segments identified by GPS coordinates, path-integrated concentrations in mg/m^2 are calculated for various species present between the sun and the system. Results can be gathered on the same map for the whole measuring itinerary, giving an overall shape of main emitting areas and associated concentrations as shown in Figure 3.43

The spectral retrieval is based on a multivariable analysis in which lab-recorded calibration spectra from literature are fitted to the actual spectra measured, for all target species but also for other interfering species like H_2O and CO_2 . Alkanes, which correspond (in mass) to the main part of refinery VOCs, are summed but cannot easily be distinguished due to spectral overlap based on common C-H bond vibration. In contrast, individual olefins can be measured with good specificity. Aromatics cannot be measured directly. In case of need, canister samples are taken at various positions downwind of the target source, and resulting mass distributions are used for the calculation of missing concentrations in the plume on a *pro rata* basis.

The overall uncertainty for quantification in industrial field conditions is evaluated [32, Mellqvist et al.2008] at around 35 – 40 %. Most of it originates from wind (speed and direction) evaluation uncertainty and retrieval uncertainty (combined effect of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect).

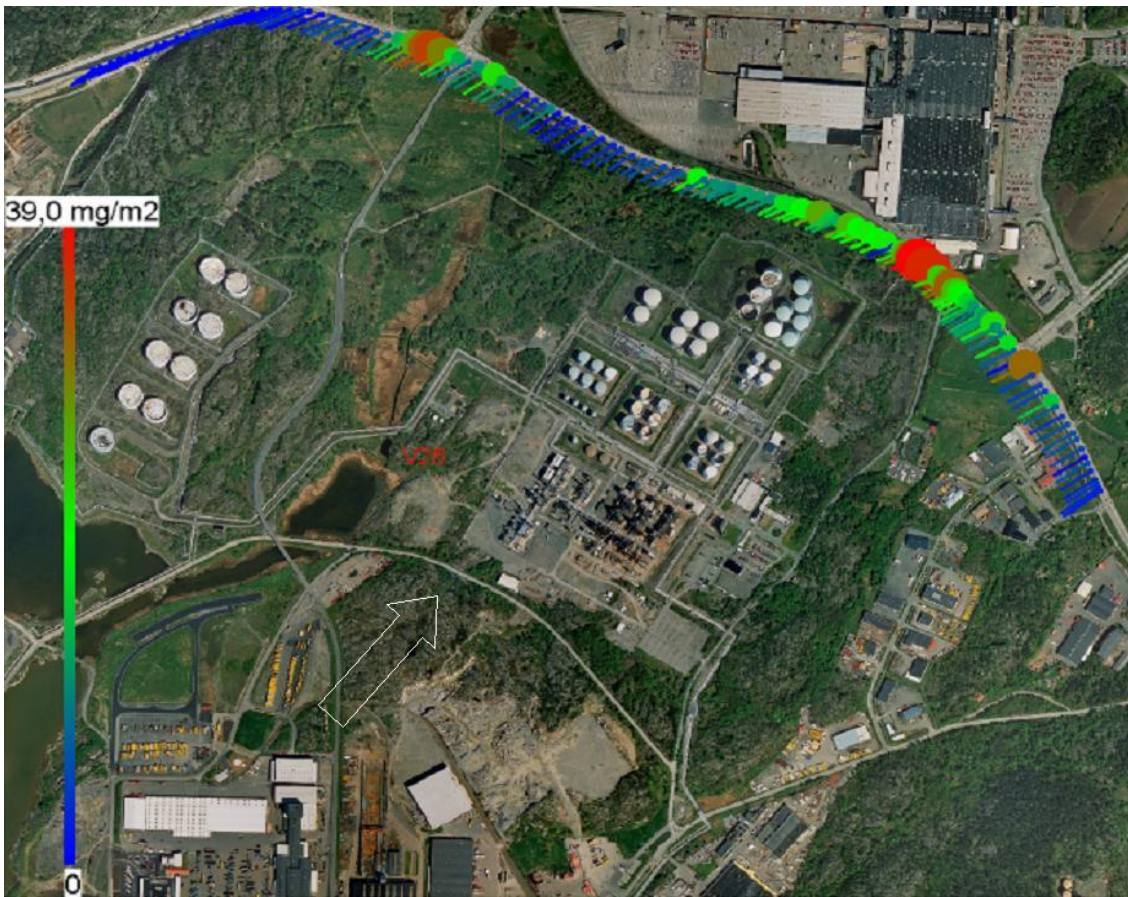


Figure 3.43: Overall shape of alkane emissions from an oil refinery as measured with SOF (the white arrow indicates the wind direction)

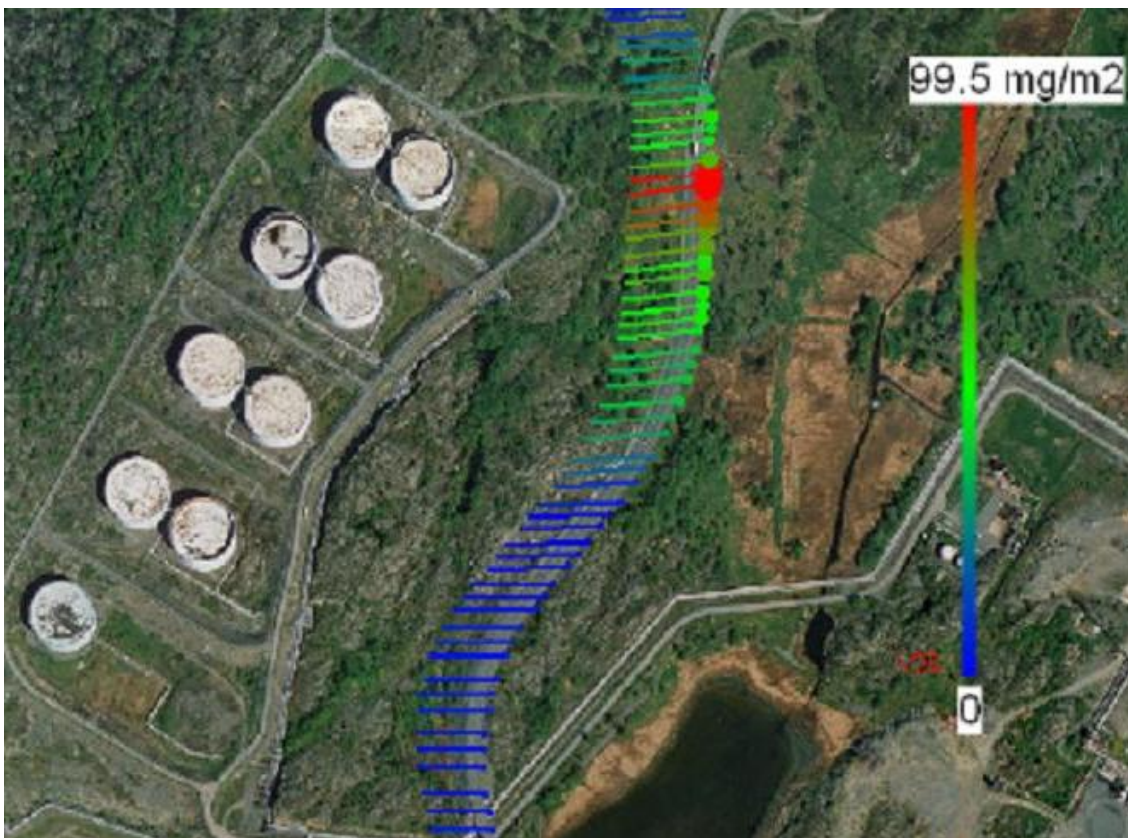


Figure 3.44: Detection of high leaking storages within a refinery tank farm using SOF

Table 3.99: Overview of performances, costs, advantages and drawbacks of diffuse VOC measuring techniques

| | Detection limit | Indicative costs (EUR) | Advantages | Drawbacks |
|-----------------|--|--|---|---|
| EN 15446 | 10 ppm at leak source <10 mg/h for correlated mass flow Increasing with wind | 5 000 – 25 000 for one detector, depending on complexity 60 000 per campaign (2 000) for a 30 000 component site 600 000 for a mini 6-month campaign in a complex refinery | Low detection limit Low instrumentation cost Applicable in hazardous/congested areas | Not applicable to diffuse area sources Direct mass flow measurement not possible Low reproducibility (standard deviation 50 %) and repeatability (standard deviation 35 %) on measured concentration Low reproducibility (standard deviation 40 %) and repeatability (standard deviation 25 %) on indirect mass flow calculations High manpower requirement and operational costs (500 components per day per surveyor) Fully applicable to components only accessible by staircases or ladders (typically around 80 %). |
| OGI | 0.4 – 60 g/h (<35mK at 30 °C) depending on operational conditions 3 000 – 10 000 ppm | 70 000 – 110 000 for one camera | High mobility Low manpower requirement (5 000 components per day per surveyor) Large monitoring scope, including remote or non-accessible large leaks detection Limited training required for operators | Presence of a background surface imperative for the active system Sensitivity related to actual thermal gradients: OGI is less efficient with uniform temperature conditions Not applicable to explosive atmospheres, but can be used under permit to work scheme; Not applicable with rain or fog. |
| DIAL | 10 – 50 ppbv at 200 m for a 50 m wide plume Increasing through dust and water vapour plumes | A single 1 – 2 week campaign costs around 30 000 – 100 000 including data processing and report Device investment >0.2 million | Well established Open path ‘single-ended’ system independent from sun direction Day and night Significant area sources can be localised with horizontal plane scanning (e.g. tank farm) Possible ‘free space’ on-site calibration using calibrated gas mixtures | Limited commercial availability Logistics (12 m long – 7 to 12 t lorry) Heavy rain and fog not suitable No precise location of individual point sources Uncertainty of mass flow calculations (wind) ‘Snap shot’ measuring: must be repeated to take into account temporal variations (e.g. tank farms) Upwind sources cannot be simultaneously determined without upstream scan (time and logistics constraints) |
| SOF | 0.5 – 1 mg/m ² 1 kg/h can be detected at 50 m distance | A single 2 week campaign costs around 60 000 including data processing and report Device investment >0.2 million | Recent but well established Well adapted to whole site estimates Significant area sources can be localised Comparatively simpler, quicker and cheaper than DIAL in favourable meteorological conditions | Limited commercial availability Only daytime and sunny conditions No precise location of individual point sources No range resolved data for alkane species No direct measurement for aromatics Uncertainty of mass flow calculations (wind + unknown VOC plume height) As for DIAL ‘snapshot’ measuring and upwind sources. |

Site-scale VOC monitoring and quantification using available measuring techniques

A number of investigations have been carried out in the US and Europe since the 1990s in order to compare the results given by conventional methods (e.g. TANKS emission factors for tank farms, EN 15446 point measuring with correlation curves for production units) with DIAL and, more recently, with SOF long-range screenings. Generally, results obtained with the latter have been shown to be higher (usual factors 2 – 5, sometimes more). Reasons were often linked to:

- results obtained with DIAL and SOF were made from extrapolated short-term measurements and have been compared to annual inventory emission estimates made by conventional methods;
- large missing sources, which were not taken into account in conventional methods (e.g. gasoline blenders in a tank farm, cooling towers, unknown leakage located in remote parts of pressurised process units, tank cleaning operations);
- underestimating assumptions about some key emission factors (e.g. flares, crude oil tanks, gas oil tanks, hot heavy fuel oil tanks) and the average mass composition of VOC mixtures (part of heavy alkanes evaporated from tanks).

However, one comprehensive study in which DIAL was used for a long, continuous period (four days), compared to a typical measurement period of a few hours, showed that there was agreement between the DIAL estimate and calculations using TANKS in the case of a new tank farm with well-maintained tanks.

In Sweden, the results of measurements undertaken with SOF and DIAL during limited periods (weeks) have been very consistent through the years.

Modern fugitive VOC monitoring should be more and more based on exhaustive screening methods and real measurements. It can also benefit from recent improvements of component-scale conventional methods together with specific opportunities introduced by short and long range optical and airborne remote techniques.

Site level monitoring of the overall VOC diffuse emissions from refineries should be derived from a well-balanced approach using all complementary techniques described below, and can be conducted mostly using the following steps.

- Fugitive emissions from leaking components can be evaluated within the implementation of a rigorous LDAR programme, using sniffing methods associated with correlation curves better established at the site level from the bagging of key equipment or, when not available, correlation curves developed for specific component types (e.g. by US EPA). Non-accessible sources are taken into account, as described in EN 15446, using these factors.
- OGI cameras should be introduced within ‘smart’ LDAR programmes for easier and faster identification of significant leaking components, in particular in remote areas, allowing for better LDAR prioritisation and focus. This includes the identification of leaks from storage tank roof seals and fittings which cannot be detected by LDAR or by DIAL/SOF technique.
- Permanent or chronic emissions from area sources (e.g. tank farms, WWTPs) still estimated from emission factors should be regularly validated by actual physical measurements, using point samplers (e.g. pumped sorbent tubes) or time correlation tracers (TCT).
- A regular full screening and quantification of site emissions undertaken with an appropriate combination of complementary methods, e.g. SOF and/or DIAL campaigns, using the results for trend evaluation in time, cross-checking and updating/validation of the ongoing LDAR programme.

Reference literature

[32, Mellqvist et al.2008], [50, White.2008], [51, Chambers et al.2006], [59, TOTAL - Béraud-Dufour, P 2009], [60, ENI - A. Selvaggi 2009], [61, INERIS 2009], [62, CONCAWE 2008]

3.26.1.4 Odour monitoring

Odour is potentially related to the emission of a large number of chemical substances and compounds. In oil and gas refining, these are most likely to be:

- **sulphur** compounds (e.g. hydrogen sulphide, mercaptans, sulphides, disulphides);
- **nitrogen** compounds (e.g. ammonia, amines);
- **hydrocarbons** (e.g. aromatics).

The perception of an odour in the surroundings of a refining plant and, eventually, the nuisance related to it, and the possibility to prevent or reduce this nuisance will depend on various parameters, highlighted below:

- The number of different sources and substances: the resulting odour from a combination of different substances can be perceived as more of a nuisance than the odour of substances emitted separately at the same concentration. Furthermore, in combination with other substances, the characteristic odour of a single substance can be modified so as to be unrecognisable.
- The olfactive thresholds of emitted substances: at the same concentration (or distance from the source), some substances will be strongly perceived as others will have disappeared. In case of a mixture, the combined odour will change as the mixture becomes diluted, until the concentration of each component falls below its own threshold.
- The individual olfactive ability and subjective reaction of exposed persons: odours can be judged as acceptable or unacceptable depending on the physical sensitivity to it, as well as on psycho-sociological factors which can influence personal preferences. For the same person, an odour can be pleasant when the substance is diluted and become offensive when concentrated.

In general, the human nose is very sensitive to certain substances or components that are typically emitted by oil and, to a lesser extent, by gas refining activities. Table 3.100 gives a selection of values according to different sources. It should be noted that most of these substances, and especially sulphur compounds, generate odours that are generally perceived as very unpleasant or aggressive.

Table 3.100: Odour thresholds of some substances and compounds typical of refining activities

| Substances or compounds | Odour thresholds | |
|--|--|--|
| | Reported ranges ⁽¹⁾ (ppm weight) | Typical ⁽²⁾ (mg/m ³) |
| Methylmercaptan CH ₃ SH | 0.000 07 – 0.004 | 0.002 1 |
| Ethylmercaptan C ₂ H ₅ SH | 0.000 008 7 – 0.002 | 0.002 77 |
| Hydrogen sulphide H ₂ S | 0.000 41 – 0.002 | 0.025 3 |
| Dimethylsulphide (CH ₃) ₂ S | 0.002 2 – 0.3 | 0.005 8 |
| Diethylsulphide (C ₂ H ₅) ₂ S | 0.002 – 0.4 | 0.001 46 |
| Dimethylamine (CH ₃) ₂ NH | 0.033 | 0.153 |
| Diethylamine (C ₂ H ₅) ₂ NH | 0.048 | 0.567 |
| Benzene C ₆ H ₆ | 1.5 – 4.7 | 11.8 |
| Ethylbenzene C ₆ H ₅ (C ₂ H ₅) | 0.17 – 2.3 | 7.3 |
| Toluene C ₆ H ₆ (CH ₃) | 0.33 – 50 | 5.95 |
| o -, m-, p-Xylene C ₆ H ₆ (CH ₃) ₂ | 0.08 – 3.7 | 1.43 – 3.77 |
| Lighter alkanes (from C ₂ H ₆ to C ₄ H ₁₀) | >50 | >500 |
| Mid range alkanes (from C ₅ H ₁₂ to C ₈ H ₁₈) | >2 | >30 |
| Heavier alkanes (from C ₉ H ₂₀) | <2 | <6 |
| ⁽¹⁾ [40, Nagata Y 1990], [42, Devos et al.1990] | | |
| ⁽²⁾ [41, ADEME 2005] | | |

Refineries should have an odour management plan as a well identified part of their environmental management system (see Section 4.15.1.1). The odour management plan should include all of the following elements:

- an odour management strategy;
- protocols for conducting odour monitoring;
- a protocol for response to identified odour events;
- an ongoing odour prevention and elimination programme designed to identify the location, nature, emission and dispersion of on-site odours, to characterise the odours, and to implement elimination and/or reduction measures in relation to these odours;
- an implementation timetable for all actions to be taken within this programme;
- reporting procedures to regularly advise management on the results of the plan;
- a review programme for regularly updating the plan.

Because odorous compounds are primarily VOCs and sulphur and nitrogen compounds, various prevention, reduction and abatement techniques already described in Section 4.23, in particular when applied to fugitive emissions, prevent and limit odour pollution. Furthermore, an overview of main odour management and treatment techniques is available in the CWW BREF [6, COM 2003].

The following sections focus on specific techniques that can be most appropriate to the oil refining sector.

3.26.1.4.1 Dynamic olfactometry with human assessors

Description

Odour concentration is determined by a panel of trained human assessors or panellists. Odour concentration is measured according to the European standard EN 13725-2003. The basis of this measurement method is that odour can be detected by a person if the individual odour threshold is exceeded, independently of the preliminary knowledge of the odorous substance concerned.

The gaseous sample of odorants is collected on site using special bags to prevent the sample from being polluted by the pumping system used to collect it. The odour concentration is determined by olfactometry, that is by presenting a panel of selected and screened human subjects with that sample, varying the concentration by diluting the sample with odour-free gas in order to determine the dilution factor at the 50 % detection threshold (that is when the odour can just barely be perceived by 50 % of the test panel). The numerical value of the odour concentration is equal to the dilution factor that is necessary to reach the odour threshold. Its unit is the European Odour Unit (ou_E). Therefore, the odour concentration at the odour threshold is 1 ou_E by definition.

The persons that are members of the panel must fulfil certain requirements, for example regarding their sensitivity to odour perception. The main panel calibration gas used to verify this requirement is n-Butanol. To ensure the required level of accuracy, odour concentration is determined by a panel composed of six to eight members. The laboratory must be ventilated to isolate the panellists from the odours in the ambient environment. Samples must be analysed within 24 hours of sampling.

Achieved environmental benefits

This method provides the necessary input for a well-established odour management plan (OMP).

Cross-media effects

None.

Operational data

No data submitted.

Applicability

The technique is fully applicable to new and existing installations.

Economics

The cost reported for one analysis is in the range of EUR 300 – 400. The cost for a complete survey including panellist training is in the range of EUR 50 000 (refinery in Spain).

Driving force for implementation

This technique is used at installations when odour nuisance is an issue or when complaints occur in the vicinity of the industrial site.

Example plants

The technique is reported to have already been used successfully for various public or industrial activities (e.g. municipal waste water treatment plants, waste elimination, animal by-products manufacturing).

Reference literature

[41, ADEME 2005], [43, INERIS 2009].

3.26.1.4.2 Odour surveys by a committee of residents**Description**

Odour nuisance is assessed by a committee of residents using different questionnaire techniques in order to evaluate the perceived nuisance. Questionnaires are filled in regularly, but always on a voluntary basis. The answers are correlated with meteorological conditions to get a link between actual emission sources and the described nuisance.

At a basic or preliminary step, the respondents are requested to rate the odour perception, the quality, and the level of nuisance on a multi-points scale. As an example, a conventional five-

point scale can include the following ratings: ‘definitely not annoying’, ‘slightly annoying’, ‘annoying’, ‘highly annoying’ and ‘extremely annoying’.

As a second step, after specific training, residents can also establish site olfactory imprints from a collection of odorous molecules organised in accordance with their dominance (e.g. amine, sulphurous, pyrazine) using recognised methodologies. One of these called ‘Le Champ des Odeurs®’ (developed by IAP Sentic) has been used since 1998 around industrial areas of the Seine estuary in France [47, AIR NORMAND 2006]. Site odour profiles are determined according to individual reference odours distributed as follows in Figure 3.45.

Conducting a survey requires enough responses to carry out a statistical analysis. Representative sampling observations (in space and time) are obtained by considering, in particular, the population density, and the direction and the velocity of the prevailing winds. The theoretical impact distances (determined by odour dispersion modelling) can also be used for sampling validation.

Achieved environmental benefits

This technique allows for a better knowledge and understanding of the conditions under which odour nuisances occur. The results can be used for adjusting plant configuration and operations to reduce odour nuisance and the parameters which have to be assessed to limit olfactory impacts can be determined. Recommendations can be proposed and circulated back to the residents, e.g. specific practices to be avoided under characteristic meteorological conditions, and main sources identified as actually a nuisance and deserving newly adapted prevention measures or abatement techniques. This improves the preparedness, participation and response of the local community potentially exposed to odour.

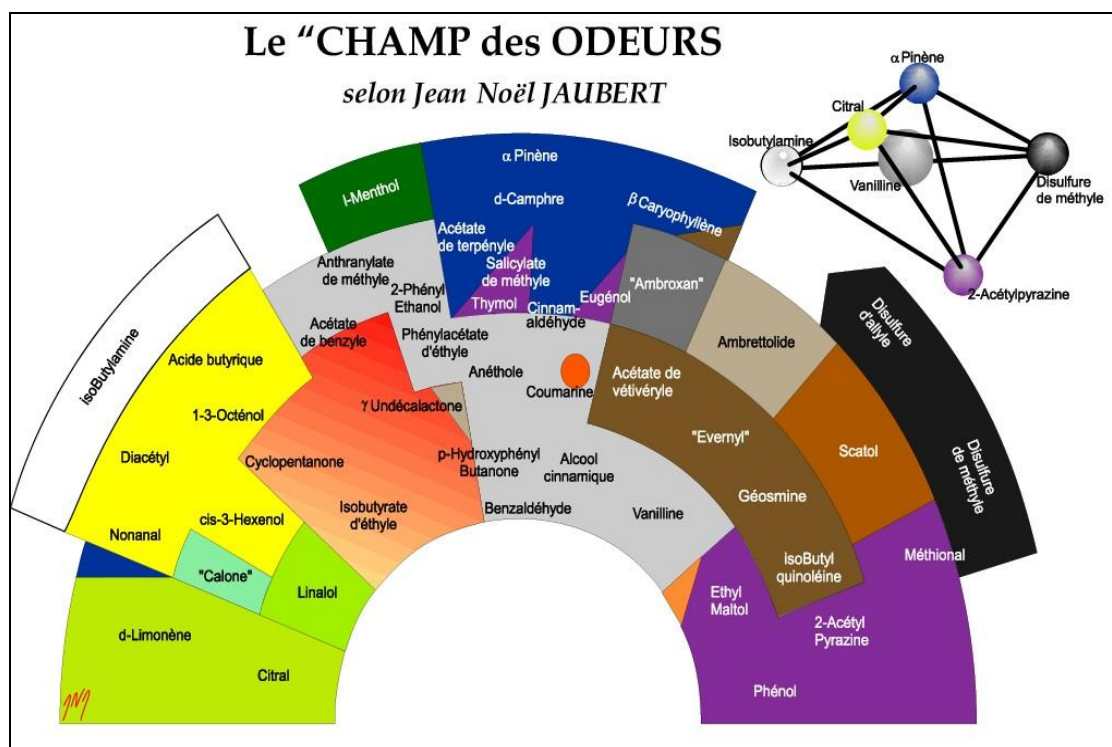


Figure 3.45: References used in a methodology for odour profile identification

Furthermore, the technique can also play a key role in the control of the effectiveness and efficiency of odour-reducing actions taken from previous monitoring campaigns. As an example, the latest olfactory profile carried out around the ExxonMobil refinery in Port-Jérôme (2006) identified a 20 % odour reduction compared to initial campaigns (1998), enabling

residents to perform by themselves a clear quantification of the results obtained from the odour-reducing action plans implemented by the refinery and neighbouring plants along this period.

Cross-media effects

There are no cross-media effects associated with the technique.

Operational data

Investigation campaigns can last quite some time (six months to one year) and require numerous observations and enough residents to be appropriately sampled on a spatial basis. As a consequence, steering resources should be put in order to ensure:

- there are enough volunteers to perform relevant statistical analysis;
- motivation of respondents during a minimal period lasting from a few months to one year, and ideally even longer in order to keep the same panel for several consecutive campaigns;
- the careful cross-analysis of all data.

In the case of the ExxonMobil refinery in Port-Jérôme (Rouen, France), typical training of residents for specific odour identification and site imprints lasts 72 hours spread over four to five months. They involve 30 external voluntary ‘noses’ living in the vicinity, together with 12 internal ‘noses’ from the refinery staff. The odour profile of the refinery has been determined as shown in Figure 3.46.

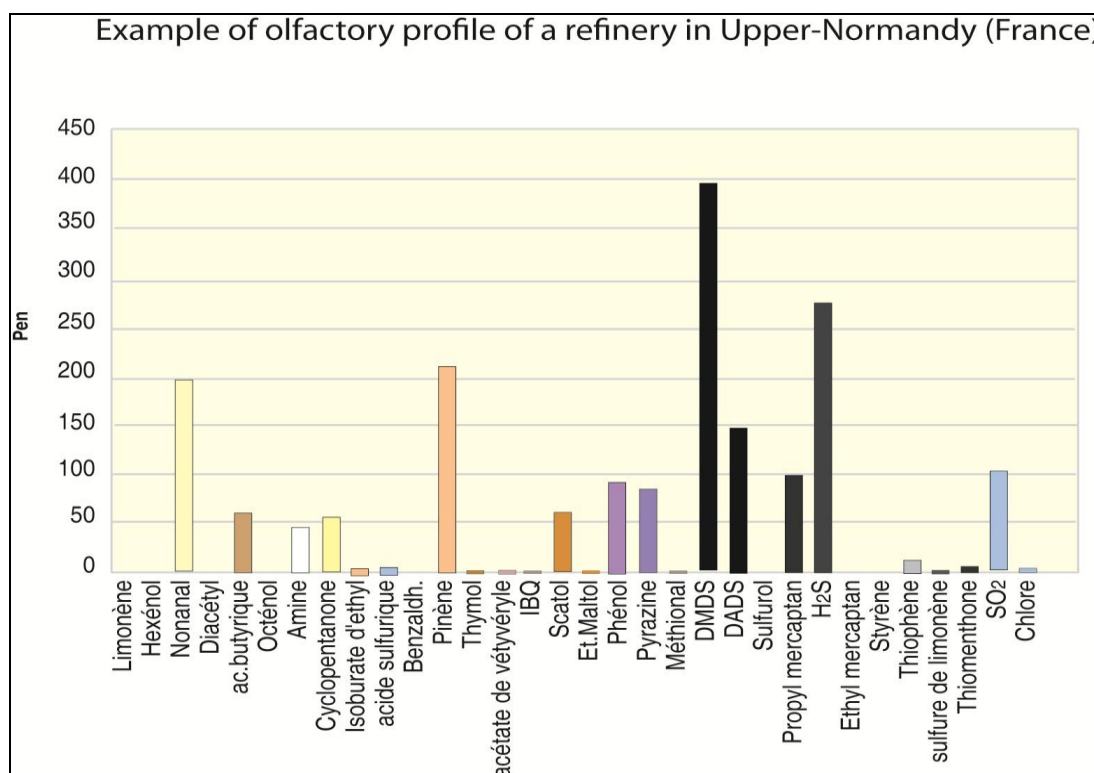


Figure 3.46: Olfactory profile of the ExxonMobil refinery in Port-Jérôme (France)

Complementary methods (such as the dynamic olfactometry described in Section 3.26.1.4.1 in particular) can be used to qualify and describe the perceived odour in order to determine the odour sources responsible for the annoyance. Implementing this technique involves setting up a training programme for the volunteers and regular debriefings.

Applicability

The technique is fully applicable to new and existing installations. As an example, over 60 industrial companies are due to have their olfactory imprints defined so far, and have their odorous impact regularly tracked along the Seine estuary industrial area.

Economics

The technique costs for an odour survey are in the range of EUR 20 000 – 30 000 for a 6-month study including the recruitment of volunteers, management of questionnaires (by post, internet or by phone), analysis of the filled-in questionnaires, and meeting management for the presentation of the results to residents and other stakeholders (specific odour identification trainings excluded).

All of this can be managed by an external consulting firm. Equipment needed generally includes a PC, statistical software, and a weather station at a cost of about EUR 10 000.

Driving force for implementation

This technique is used at installations when odour nuisance is an acute issue, in order to provide the necessary input for a well-established odour management plan (OMP). It will help to solve complaints and to build up and maintain constructive relationships between the operator and the residents.

Example plants

The technique is reported to be used in several industrial areas in France, where oil and petrochemical plants in particular are in operation.

Reference literature

[44, INERIS 2009], [47, AIR NORMAND 2006], [49, ExxonMobil 2009]

3.26.2 Monitoring of releases to water

Continuous monitoring and flow-proportional sampling for releases to water are always preferable but the use of a fixed interval or time-proportional sampler for low flow rates (less than 1 litre per second) may be acceptable.

The monitoring of process effluents released to controlled waters and sewers will commonly be carried out for the following: flow rate, pH, temperature, and TOC (surrogate for COD/BOD). Samples are also being monitored for other appropriate parameters such as COD, BOD, Total Petroleum Hydrocarbons, suspended solids, nitrogen compounds, phenols, benzene, metals (typically Cd, Hg, Ni, and Pb). The periodicity can be typically daily, weekly or monthly, depending on the risk assessment and on local circumstances.

One problem with effluent discharge monitoring from refineries is related to the analytical method. For example, for the analysis of petroleum hydrocarbons (oil) there are many different methods (e.g. GC-MS, IR one wavelength, IR two wavelengths, gravimetric) which give completely different results which prohibit a clear comparison. Unification of analytical methods or calibration against a standard preferred method can circumvent this issue.

3.26.3 Monitoring solid wastes

A recording of the quantity and composition (including prescribed substances) of residues generated is typically carried out. In addition, the operator typically has written procedures which ensure that releases are handled, treated and disposed of in an approved manner, and which specify how the accumulation and storage of waste are to be controlled. The frequency of analysis of the waste is site-and/or process-specific.

3.26.4 Soil and groundwater monitoring

Groundwater is an important resource and is protected from deterioration and pollution. In Europe, protecting groundwater is addressed through the Water Framework Directive (2000/60/CE establishing a framework for Community action in the field of water policy) and its daughter Directive (2006/118/CE on the protection of groundwater against pollution and deterioration).

As groundwater may be an important way of transfer for pollutants, the implementation of a groundwater monitoring network around industrial sites which could be at the origin of pollution is essential. Therefore, the protection of this environmental compartment is integrated into the location's environmental management plan which includes the prevention of spills that could lead to groundwater contamination and a response plan to deal with unforeseen incidents.

Moreover, the collection of data on groundwater quality and quantity on a regular basis helps warn in the case of unnoticed accidental or chronic pollution, and will allow corrective control measures, if required. In addition, it is considered normal practice to install a groundwater monitoring system within the site's boundary to warn of groundwater contamination before it reaches the site boundary or enters the site from neighbouring installations. An example of soil and groundwater monitoring is provided in Annex 8.5 below.

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this document. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers environmental management systems, process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations).

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 4.1 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied in the sector. Other techniques may exist, or may be developed, which could be considered for the determination of BAT for an individual installation.

Table 4.1: Information for each technique described in this chapter

| Headings within the sections |
|--|
| Description |
| Technical description |
| Achieved environmental benefits |
| Environmental performance and operational data |
| Cross-media effects |
| Technical considerations relevant to applicability |
| Economics |
| Driving force for implementation |
| Example plants |
| Reference literature |

This chapter should be seen as the main background information for the determination of best available techniques in the refinery sector (Chapter 5). Techniques that are generally seen as obsolete are not included. Moreover, this chapter does not include all the techniques applied in the refinery sector and described in Chapter 2. Only techniques with good environmental performance are included here.

Production, prevention, control, minimisation and recycling procedures/techniques are considered in this chapter. These techniques/procedures can be carried out in many ways, such as using production techniques that pollute less than others, changing the operating conditions, reducing material inputs, re-engineering processes to reuse by-products, improving management

practices or employing substitution of toxic chemicals. This chapter provides information on some general and specific pollution prevention and control advances that have been implemented within industry in general and in the refinery industry in particular.

As in Chapters 2 and 3, each section of this chapter deals with a refinery process or activity and contains the process and abatement techniques worth considering in the determination of BAT. If different techniques are applicable for one process/activity, they are discussed in the respective process activity section. Sections 4.2 to 4.22 in this chapter have been structured in the same way. Each of these sections contains first the pollution prevention primary techniques applicable in the process/activity section referred to, and second the end-of-pipe (EOP) techniques that may be applicable for reducing the emissions for the process/activity. The EOP techniques are grouped into media/pollutant categories to clarify the sequence of techniques applicable. In some cases, the number of EOP techniques that may be used is quite extensive.

At the end of this chapter, three sections appear containing the EOP techniques applied to waste gas, waste water and waste management. These sections contain the descriptions of the EOP techniques that may be applicable to more than one refinery process/activity, as well as some other EOP processes. Consequently, the descriptions of the EOP techniques that may appear in this chapter are included in Sections 4.23, 4.24 and 4.25 and not in the activities/processes sections.

4.1 General overview

Table 4.2 gives the number of techniques considered in the document for each refining activity or process described. These techniques have been split into four categories. The numbers included in this table are only indicative and are not the simple recounting of the subsections. As will be seen, some subsections include more than one technique. This table is only meant to give an overview of the number of techniques considered in each section of the document, as a first indicator of what activities/processes are more important from the environmental point of view (e.g. energy system, storage and handling, integrated management, catalytic cracking, coking).

Table 4.2: Number of techniques (or families of techniques) addressed in Chapter 4

| Chapter section | Activity/process | Number of techniques applied to: | | Total |
|-----------------|--|----------------------------------|-------------|------------|
| | | Production and prevention | End-of-pipe | |
| 2 | Alkylation | 3 | - | 3 |
| 3 | Base oil production | 8 | 2 | 10 |
| 4 | Bitumen production | 2 | 5 | 7 |
| 5 | Catalytic cracking | 6 | 11 | 17 |
| 6 | Catalytic reforming | 1 | 3 | 4 |
| 7 | Coking processes | 21 | 12 | 33 |
| 8 | Cooling systems | 3 | - | 3 |
| 9 | Desalting | 13 | 4 | 17 |
| 10 | Energy system | 57 | 8 | 65 |
| 11 | Etherification | 3 | - | 3 |
| 12 | Gas separation processes | 2 | - | 2 |
| 13 | Hydrogen-consuming processes | 4 | - | 4 |
| 14 | Hydrogen production | 4 | - | 4 |
| 15 | Integrated refinery management | 13 | - | 13 |
| 16 | Isomerisation | 2 | - | 2 |
| 17 | Natural gas plants | 15 | 6 | 21 |
| 18 | Polymerisation | 3 | - | 3 |
| 19 | Primary distillation units | 21 | 2 | 23 |
| 20 | Product treatments | 4 | - | 4 |
| 21 | Storage and handling of refinery materials | 21 | - | 21 |
| 22 | Visbreaking and other thermal conversions | 3 | 1 | 4 |
| 23 | Waste gas minimisation and treatments | 5 | 22 | 27 |
| 24 | Waste water treatments | 8 | 17 | 25 |
| 25 | Waste management | 12 | 2 | 14 |
| | TOTAL | 234 | 95 | 329 |

4.2 Alkylation

Three alkylation processes are considered in the determination of BAT: the hydrofluoric acid (HF), the sulphuric acid (H₂SO₄) and the solid-acid process. As the third process is still considered an emerging technique, it is described in Chapter 6.

4.2.1 Hydrofluoric acid alkylation process

Description

A brief description of this process can be found in Section 2.2.

Achieved environmental benefits

The main advantages of the HF alkylation process in comparison with the sulphuric acid process are the regeneration of HF, which minimises waste formation and disposal, and the lower acid catalyst consumption, as well as the minor consumption of energy and cooling.

Cross-media effects

Effluent gases

A scrubber using alkaline solution (NaOH or KOH) is necessary to remove HF from the incondensable gas stream. The acid relief neutraliser is operated so as to minimise the hydrogen fluoride content of the incondensable gas stream. Concentrations of less than 1 mg HF/Nm³ can be achieved. The vent gas can then be passed to flare, not to the refinery fuel gas system. A dedicated flare/stack is normally retained for this but, depending on the gas' composition, it is reported that it may be vented to a non-dedicated flare/stack (e.g. operation at a Spanish refinery). Fugitive emissions are also generated by this process.

HF is a *very dangerous compound* because of its severe corrosive nature and the burning effects of both liquid and fumes on the skin, eyes and mucous membranes. Consequently, storage and handling should comply with all safety rules.

KF (or NaF) is formed during the neutralisation process. The spent solution is stored and then requires regeneration with lime. The regenerated KOH is recycled but typically NaOH is not. CaF₂ is regularly cleaned out and disposed of, usually to a landfill. Fumes can originate in the neutralising basin unit. To prevent the discharge of these odorous gases to the surroundings, the neutralising basins are tightly covered and equipped with a gas scrubber to remove any offensive agents.

Water

HF alkylation effluents are a potential cause of acid excursions in refinery effluents and a high standard of control should be exercised on the neutralisation treatment system, e.g. on-line pH monitoring. The effluent containing HF acid can be treated with lime (CaO-Ca(OH)₂), AlCl₃ or CaCl₂ or it can be neutralised indirectly in a KOH system to produce the desired CaF₂ or AlF₃ (insoluble) which is separated in a settlement basin. The supernatant liquor flows to the water treatment process. KOH may be regenerated for reuse. After this treatment, the supernatant still contains 10 – 40 ppm F and some hydrocarbons, and is directed to the WWTP. KOH may be regenerated from the aqueous solution for reuse.

Wastes

The HF process also yields tars (polymeric material) but these are essentially free from HF. HF-containing tars are neutralised and disposed of by incineration or blended as a fuel oil component, usually in small amounts because of its pronounced odours. However, technology and special operating techniques such as internal acid regeneration have significantly reduced this liquid waste stream.

Poor operation of the system (excessively cold acid, improper acid settler level, low reactor pressure, excessive acid recycling rate, low i-butane or acid concentration, high reactor temperature and improper mixing) increases the amount of waste generated.

Operational data

The potentially corrosive and toxic properties of HF necessitate special engineering design and special construction materials, advanced process controls and stringent safety, personnel protection and maintenance requirements. These precautions include:

- special seals on acid-containing equipment such as pumps and valve stems;
- special safety clothing which must be worn by personnel entering an acid area;
- extensive operator training;
- special facilities (e.g. sprinkler systems, acid-inventory reduction, HF detection systems, isolation valves, rapid acid transfer systems) should be included in the design of this kind of system to mitigate the effects of an accidental emission of HF vapour clouds. For leak detection, HF-sensitive colours on pipes and flanges are suitable as alternatives to continuous air analysers and video control. The potential reduction of aerosol formation of HF acid has also been demonstrated by using an additive-based system. Special care should be taken during maintenance and cleaning of the plant, e.g. for major shutdowns, not to release odours from the drainage system and/or ponds.

The same developments (such as additives) have already been tested in order to lower the vapour pressure and to minimise the amount of HF released to the atmosphere in case of an accident. The downside of this is that handling and recycling the additive add to the complexity of the process.

Applicability

Fully applicable.

Economics

Table 4.3 shows the investment and production cost summary for HF alkylation. Disposal costs are not included.

Table 4.3: Examples of investment and operational costs for a HF alkylation unit

| Costs | Estimated erected cost (3 rd quarter 1995) | New HF plant (1999) |
|---|--|------------------------|
| Investment cost | | |
| Capacity (kt alkylate/yr) | 348 | 160 |
| Investment cost (EUR million) | 25.6 | 35 |
| Operating cost (EUR/tonne alkylate) | | |
| Labour | 0.016 | |
| Utilities | 0.066 | |
| Chemical consumption, laboratory allowance, maintenance, taxes and insurance | 0.056 | |
| Total direct operating costs | 0.138 | |

Driving force for implementation

Alkylation is a refinery process used to increase gasoline octane. Safety requirements due to HF are the main environmental driver for this process.

Example plants

HF alkylation is very widely used.

Reference literature

[164, Noyes 1993], [175, Meyers 1997], [204, Canales 2000], [207, TWG 2001]
[240, Hommeltoft 2000].

4.2.2 Sulphuric acid alkylation process

Description

A brief description of the process can be found in Section 2.2.

Achieved environmental benefits

Sulphuric acid is an alternative process for alkylation, but has the drawback of more spent acid, which must be regenerated, typically outside the plant installation. The efficiency of the process is lower than with HF alkylation and more cooling is needed.

Cross-media effects

Technologies using sulphuric acid as a catalyst produce very large quantities of spent acid (sulphuric and sulphonic acids) that have to be regenerated. The transport of spent and fresh acid to and from the sulphuric acid regeneration unit has given rise to some concern and has increased pressure on refiners to establish sulphuric acid regeneration plants near alkylation units. In some cases, this transport to/from the regeneration facility is by pipeline. However, no major new improvements have been introduced in sulphuric acid alkylation technology dealing with the spent acid issue. Fugitive emissions from this process are similar to those from HF alkylation.

Acid-soluble oil is continuously generated as a by-product of sulphuric acid alkylation. This oil goes into the acid phase and dilutes the strength of the acid within the unit, unless a portion of the acid is continuously purged (spent acid) and replaced with fresh acid. The spent acid containing the acid-soluble oil is sent to the regeneration process on site, through the acid regenerator unit, or off site. Tars from the H₂SO₄ process contain sulphuric and miscellaneous sulphonic acids, which may cause disposal problems. In addition to spent acid, this process generates spent caustic and alkaline waste water streams, which must be sent to a WWTP or to possible regeneration (in the case of the caustic). Depending on BOD and COD requirements at the WWTP, the waste water stream may require a nitrogen stripper to remove dissolved hydrocarbons.

Operational data

The product quality from butylene (primary feedstock) is higher than in HF alkylation. To produce an equivalent product quality, HF alkylation would require similar energy consumption to sulphuric acid alkylation. As sulphuric acid is less toxic than HF and does not form a vapour cloud if released, this type of process is often considered to be safer. However, the actual determination of risk level is site-specific and has to be carried out within a specific risk assessment methodology.

Table 4.4: Example of utility and chemical consumption for H₂SO₄ alkylation

| Utilities and chemical consumption (based on 716 m ³ /d alkylate plant) | |
|---|-------|
| Power, kW | 1 779 |
| Compressor | 1 235 |
| Pumps | 303 |
| Mixers | 240 |
| Cooling water, m ³ /h ⁽¹⁾ | 835 |
| Industrial water, t/d | 39 |
| Steam, kg/h | |
| 3.45 barg | 13 |
| 10.3 barg | 3 |
| Chemicals | |
| Fresh acid, t/d ⁽²⁾ | 40 |
| NaOH -15 Baume ⁽³⁾ , t/d | 1.7 |
| ⁽¹⁾ Cooling water supply temperature is 26 °C and the average ΔT is 15 °C. | |
| ⁽²⁾ Includes allowance for feed impurities. | |
| ⁽³⁾ 15 'degrés Baumé' ≈10 % w/w. | |

The sulphuric acid removed needs to be regenerated in a sulphuric acid plant which is generally not a part of the alkylation unit and is normally located off site.

Applicability

Fully applicable. From the economic point of view, this alkylation process is mostly driven by the proximity of a regeneration facility for sulphuric acid.

Economics

Some data are available in Table 4.4 and Table 4.5.

Table 4.5: Examples of investment and operational costs for H₂SO₄ alkylation

| Capacity | Estimated costs | Units |
|--------------------------|---|--|
| 290 kt/yr | Material USD 12.0 million Labour USD 1.7 million | US Gulf Coast, 2nd quarter 1993. Operational data correspond to this plant. |
| 28 300 m ³ /d | USD 14.49 million | |
| 1 590 m ³ /d | USD 22 000 per m ³ /d | US Gulf Coast, 4th quarter 1998 |

Driving force for implementation

Alkylation is a refinery process used to increase the gasoline octane.

Example plants

Sulphuric acid alkylation is widely used.

Reference literature

[175, Meyers 1997], [183, HP 1998], [207, TWG 2001], [240, Hommeltoft 2000].

4.2.3 Upgrade feedstock by selective hydrogenation or isomerisation

Description

More information about the processes can be found in Sections 2.13, 4.13.4, 2.16 and 4.16.

Achieved environmental benefits

The naphtha hydrotreatment or isomerisation (e.g. hydrogenation of butadiene, isomerisation of 1-butene to 2-butene) helps the alkylation units to reduce the acid losses and consequently the waste generation. As a consequence, the amount of caustic consumed is decreased. The reduction in acid and caustic consumption depends on the feed diene (diolefin) content, which varies widely at different refineries.

Cross-media effects

Drawbacks for the implementation of such a technique include the increased fuel/energy consumption, the increased fugitive emissions and the need for spent catalyst handling to be used in such a process. More information about these issues can be found in Sections 4.13 and 4.16.

Operational data

This technique requires hydrogen and consumes energy.

Applicability

There are no restrictions on the application of this technique.

Economics

See Sections 4.13 and 4.16.

Driving force for implementation

Because of the increased demands for higher octane gasoline and the increased conversion of heavier crudes to lighter products, there has been a relative decrease in the quality of alkylation feed throughout the industry.

Example plants

No information provided.

Reference literature

[164, Noyes 1993], [207, TWG 2001]

4.3 Base oil production

As described in Section 2.3, several types of processes can be found in the base oil production. They include the deasphalting unit, aromatic extraction, high-pressure hydrogenation unit, dewaxing, hydrofinishing and wax processing. All of these processes are covered here and the good techniques from the environmental point of view are discussed in this section. Techniques applicable for the storage of the solvents used in base oil production (e.g. furfural, NMP, MEK, MIBK) and intermediates are also included here.

4.3.1 Multiple-effect extraction process

Description

Solvent-based processes used in the manufacture of base oils are energy-intensive because large volumes of solvent must be recovered by flash distillation for recycling back to the process. The number of stages used for evaporation of the solvents has a significant effect on the energy cost for these processes and as many as five evaporation stages were used in some early liquid SO₂ extraction units in Europe.

Achieved environmental benefits

Heat efficiency can be improved (less water and steam usage) by applying 'double and triple effect configurations', especially in the deasphalting and aromatic extraction units. Energy saving for triple effect evaporation is 30 – 33 % compared with double effect evaporation.

Cross-media effects

None in particular.

Operational data

Utilities needed for this process are listed in the economics section below. The energy saving for the triple effect system is on the low-level heat side only (in most cases LP steam) where refineries often already have a surplus. This means that the actual savings depend on the local circumstances and a retrofit/change should be evaluated for each individual location.

Applicability

Multiple-effect evaporation requires both a pressure and a temperature driving force. In some instances, the increase in pressure and temperature required to go from the double to triple effect is not feasible and could result in higher emissions and energy consumption because of the larger residual amounts of solvent left in the oil leaving the evaporation section and entering the stripping section.

Triple effect systems are typically used for non-fouling feedstocks only (e.g. wax), as they are known to be more vulnerable in this respect, so their application is restricted.

Economics

An order of investment costs (based on a 318 – 6 360 m³/d capacity range) was around USD 5 000 – 18 900 per m³/d (4th quarter 1998, US Gulf). An example of comparative costs for single, double and triple effect options is given in Table 4.6.

The number of stages used for evaporation of the solvents has a significant effect on the energy cost for these processes. As many as five evaporation stages have been used in some early liquid SO₂ extraction units in Europe. Double effect units are the predominant type of evaporation process, but since around 1980 most new units have been designed for triple effect evaporation to reduce the cost of energy consumption. Some existing units have been converted. Heat efficiency can be improved (less water and steam usage) by applying double and triple effect configurations, especially in the deasphalting and aromatic extraction units.

The energy saving for the triple effect system is on the low-level heat side only (in most cases LP steam) where refineries often have a surplus. This means that the actual savings depend on the local circumstances and a retrofit/change should be evaluated for each individual location.

Table 4.6: Economics related to energy savings for three multiple-effect deasphalting options

| Type of cost | Single effect | Double effect | Triple effect |
|--|---------------|---------------|---------------|
| Conversion investment, USD ⁽¹⁾ | 0 | 1 300 000 | 1 900 000 |
| Annual utility cost, USD ⁽²⁾ | | | |
| Medium-pressure steam, USD 8.1/t | 91 100 | 91 100 | 91 100 |
| Low-pressure steam, USD 6.8/t | 931 600 | 465 200 | 377 500 |
| Power, USD 0.04/kWh | 218 400 | 218 400 | 218 400 |
| Cooling water, USD 0.018/m ³ | 87 200 | 47 600 | 39 200 |
| Fuel, USD 1.92/net GJ | 44 100 | 44 100 | 44 100 |
| Total annual utility costs | 1 372 400 | 866 400 | 770 300 |
| Annual utility reduction | 0 | 506 000 | 602 100 |
| ⁽¹⁾ Estimated basis: United States Gulf Coast, 3rd quarter 1995. ⁽²⁾ Based on unit cost provided by SRI International, Menlo Park, CA (US). December 1994. NB: Large savings are shown for low-pressure steam. In most refineries, low-pressure steam is considered 'free' since excess is vented to the atmosphere. | | | |

Driving force for implementation

The conversion to a multiple-effect unit reduces the utility cost.

Example plants

Multiple-effect extraction is a common technology used in refineries with lubricant oil production. Double effect units are the predominant type of extraction processes. Units built from 1950 to 1975 used double effect and a few used single. Because the cost of energy increased rapidly during the 1970s, most new units built since around 1980 have been designed, and older units have been converted, for triple effect evaporation, to reduce the cost of energy consumption.

Reference literature

[175, Meyers 1997], [183, HP 1998], [231, Sequeira 1998].

4.3.2 Conversion of a solvent extraction unit (from Furfural or Phenol to NMP)

Description

The selection of the type of solvent used in aromatic extraction has an impact on the energy consumption of the process. Moreover, a lower footprint solvent, like furfural or n-methylpyrrolidone (NMP), can be used instead of a more hazardous selective solvent like phenol, cresol or sulphur dioxide. The relevant characteristics of the mainly used solvents are presented in Table 4.7.

Achieved environmental benefits

The use of a less polluting solvent (e.g. NMP or furfural) has a positive effect on the reduction of emissions of phenols and sulphur dioxide in the refinery effluents.

Compared to phenol, NMP has faster settling rates and a lower specific heat, requiring less energy for solvent recovery. Compared to furfural, NMP is more thermally and chemically stable, more selective, requires less energy for recovery, and avoids the need for a feed deaerator. [133, EXXON 2012]

Additional advantages of the use of furfural or NMP include a higher selectivity leading to a higher raffinate yield and a lower solvent ratio, which both result in a lower energy consumption by some 30 – 40 %.








Cross-media effects

Care should be taken to avoid solvent contamination of aqueous effluents by applying efficient solvent recovery techniques. Some contamination of aqueous effluents occurs, so care should be taken not to upset the downstream biological treatments. NMP is easier to degrade in the WWTP than furfural, however it is also more corrosive than clean furfural (NMP is corrosive when feed is not properly pretreated).

Operational data

The performance of NMP and furfural techniques are similar. Well maintained and operated furfural extraction units perform just as well as NMP plants. Similar quantities of furfural, as for NMP, are required when the plants are run in the correct manner

Table 4.7: Characteristics of some of the mainly used solvents for base oil production

| | Aromatic extraction | | | Solvent dewaxing | | | |
|--|--|---|--|---|---|--|--|
| Short name | NMP | PHENOL | FURFURAL | Me | Di | MEK | MIBK |
| Composition | C ₅ H ₉ NO | C ₆ H ₆ O | C ₅ H ₄ O ₂ | CH ₂ Cl ₂ | C ₂ H ₄ Cl ₂ | C ₄ H ₈ O | C ₆ H ₁₂ O |
| Name | N-Methyl-2-pyrrolidone | Phenol | Furfural | Dichloromethane | 1,2-Dichlorethane | Methyl ethyl ketone | Methyl isobutyl ketone |
| CAS number | 872-50-4 | 108-95-2 | 98-01-1 | 75-09-2 | 107-06-2 | 78-93-3 | 108-10-1 |
| Indication of danger | T  | T  | T  | Xn  | F, T  | F, Xn  | F, Xn  |
| Toxicity | | R 32/24/25 Toxic by inhalation, in contact with skin and if swallowed | R23/25 Toxic by inhalation and if swallowed | | | | |
| Effects | R 36/37/38 Irritating to eyes, respiratory system and skin | R 34 Causes burns | R 36/37/38 Irritating to eyes, respiratory system and skin | | R36/37/38 Irritating to eyes, respiratory system and skin | R 36 Irritating to eyes | R36/37 Irritating to eyes and respiratory system |
| Harmfulness | | R 48/20/21/22 Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed | R 21 Harmful in contact with skin | | R22 Harmful if swallowed | | R 20 Harmful by inhalation |
| Long-term effects Mutagenic Carcinogenic | R61 May cause harm to the unborn child | R68: Possible risk of irreversible effects | R40 Limited evidence of a carcinogenic effect | R40 Limited evidence of a carcinogenic effect | R45 May cause cancer | R66, R67 | R66 |

Source: European Commission [134, COM 2012]

Applicability

Some technical restriction for applicability of change of solvent when switching to NMP from phenol is reported due to the following: NMP has a higher boiling point (by 22 °C), a lower melting point (by 64 °C) and no azeotrope. For these reasons, furfural is typically used when producing lower boiling point base oils (e.g. transformer oil distillates).

Major modifications would be required for existing units to change from furfural to NMP as the process conditions are different (for example a change from hot oil heat exchangers to a fired furnace to achieve the required temperatures in the solvent recovery section).

Nevertheless, the lower viscosity of NMP gives a higher throughput for a given size tower. This results in lower construction costs and reduced energy and operating costs. Raffinate oil yields average 3 % to 5 % higher for the NMP extraction and with more stable and reliable plant operation, including at lower treatment rates. It enables safer operations by using less toxic solvent and simplified solvent recovery. This conversion to NMP is applicable to the extraction of both paraffinic and naphthenic feedstocks and therefore makes it an attractive solution for the extraction of lubricating oil stocks.

Economics

Costs for switching from one solvent to a more favourable one will have to be evaluated on a case-by-case basis. In some cases, the change of solvent used does not entail significant extra costs. On the other hand, the change from SO₂ aromatic extraction to any other solvent requires a completely new unit.

The switch from a furfural to an NMP process requires economic calculations because major modifications may be required. As a consequence, the energy saving against the cost of the revamp has to be weighed on a case by case basis. Changing from furfural to NMP requires significant investment, including, but not limited to, the extraction tower, furnaces, metallurgy, etc.

The cost for the conversion of a phenol unit to an NMP unit (100 m³ per operating day - feasibility study) is estimated at EUR 4.15 million (CSZ 100 million). Other estimates show that the investment costs to switch from a phenol unit to an NMP unit is around 70 % of the cost of a completely new unit.

A cost comparison for major base oil refining processes is given in Table 4.8.

Table 4.8: Basic cost comparison between three aromatic extraction processes

| Costs | Furfural | NMP | Phenol |
|-------------------|----------|-----|--------|
| Solvent, relative | 1.0 | 2.3 | 0.60 |
| Investment | Medium | Low | High |
| Maintenance | Medium | Low | High |
| Energy | High | Low | Medium |

Driving force for implementation

Reduction of energy consumption (25 – 50 % less solvent loss due to easier solvent recovery) and of the emission of phenols and SO₂ in the refinery.

Example plants

Furfural and NMP solvent extraction processes are common technologies.

Reference literature

[133, EXXON 2012], [134, COM 2012], [135, Abdul-Halim A et al.2009], [162, HMIP UK 1993], [207, TWG 2001], [231, Sequeira 1998], [252, Ullmann's 2012].

4.3.3 Solvent recovery from dewaxing units

Description

Information about the process can be found in Section 2.3. The following prevention techniques may be applied to the solvent dewaxing process:

- Including vapours from the wax filters in the inert gas system by circulating the inert gas, and recovering solvent vapours by refrigeration as part of the process. Solvent incineration in furnaces should be minimised. An alternative to refrigeration is the pressure absorption of solvents in oil (e.g. fresh feed or finished).
- Using solvents for the process, including propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK). Toluene (associated with a risk phrase, R63: Possible risk of harm to the unborn child) or chlorinated hydrocarbons (this large family includes substances with a significant toxicity to humans and a high persistence in the environment) should be avoided. As described in Section 2.3, the chlorinated solvents used may be a mixture (DiMe) of 1,2-dichloroethane (DCE) and dichloromethane (DCM).
- Sending solvent-contaminated water resulting from the solvent recovery stage to the WWTP.
- Using inert gas, in place of steam, for stripping the last traces of solvent from the dewaxed oil and waxes. When chlorinated solvents are used this procedure is typically applied.

In wax-processing units, solvent recovery (e.g. for DCE) is carried out using two systems: one for the de-oiled wax and another one for the soft wax. Both consist of heat-integrated flash drums and a vacuum stripper. Streams from the dewaxed oil and waxes product are stripped for removal of traces of solvents. This step of the process can be carried out by inert gas stripping or steam stripping.

In MEK and toluene solvent dewaxing units, inert gas is used for stripping. The solvent can be kept water-free and efficiently recovered from the contaminated inert gas flow arising.

In DiMe units, steam stripping combined with a condensation stage is commonly used to remove the solvents from the products. The water can be treated efficiently within the process to separate the solvent. The solvent is then recovered and kept in the system.

Achieved environmental benefits

Maximising the recovery of the solvents used in the solvent dewaxing processes reduces the contamination of waste water by toluene or chlorinated hydrocarbons. The benefits of inert gas stripping in solvent dewaxing are the reduction of energy requirements in solvent refining units, the increase of dewaxed oil yields, reduction of the dilution ratios, reduction of solvent losses, decrease of the dewaxing differential, and maintenance cost reduction.

Cross-media effects

Large refrigeration systems are used and refrigerant losses from these should be minimised. Energy consumption is increased for refrigeration/pressure and heat. Care should be taken to avoid solvent contamination of aqueous effluents because most of the solvents used in solvent dewaxing are problematic for water microorganisms and waste water plants. VOC fugitive emissions may be generated during the processes.

Operational data

Table 4.9 gives some data on typical utility specific consumption for dewaxing solvent recovery units.

Table 4.9: Typical specific utility consumption for dewaxing solvent recovery units

| Utilities per m ³ feed | | Units |
|-------------------------------------|-------|----------------|
| Fuel | 1 856 | MJ |
| Electricity | 290 | kW |
| Steam | 171 | kg |
| Cooling water ($\Delta T = 25$ °C) | 36 | m ³ |
| Solvent make-up | 1.7 | kg |

Applicability

Generally applicable to new units. Existing units would require a feasibility study due to the specificity of the processes used which are generally designed for a specific type of solvent.

Economics

A new solvent recovery unit cost USD 66 000 per m³/day (based on 44 000 m³/day feed rate capacity, 1998, US Gulf Coast). Data on the implementation of inert gas stripping in refineries showed payback times of 9 – 14 months.

Driving force for implementation

Solvent recovery from dewaxing can be used in refineries that have solvent dewaxing units in their lubricant oil production processes to promote the reduction of solvent losses.

Example plants

Many refineries with lubricant production have these types of processes.

In recent years, several furfural extraction plants have been converted into NMP plants.

Reference literature

[148, Irish EPA 1993], [183, HP 1998], [207, TWG 2001], [231, Sequeira 1998].

4.3.4 Wax reprocessing unit**Description**

Hydrofinishing or clay treating can be used in wax processing.

Achieved environmental benefits

Wax hydrofinishing offers several advantages over clay treating, including lower operating costs and the reduction of waste generation.

Cross-media effects

When hydroprocessing is used, hydrogen is necessary. Hydrotreatments consume energy, hydrogen and nickel, tungsten or even platinum catalysts. Spent clay needs to be appropriately disposed of.

Operational data

Hydrogen finishing yields are close to 100 %, whereas the clay treating product yield ranges from 75 % to 90 % for the microcrystalline waxes, and as high as 97 % for light paraffin waxes. Hydrogen consumption is around 15 Nm³ per m³ of wax produced. Clay consumption runs from 2 to 45 kg/t of product.

Applicability

Hydrofinishing is fully applicable especially when hydrogen is available. However, in some cases, hydrofinishing processes cannot achieve certain special product quality specifications.

Economics

Investment costs for a wax hydrofinishing process are in the range of EUR 1.4 – 2.3 million for a feed capacity of 20 000 t/yr (from an average USD 3 500 – 5 700/bpd depending on pressure level and size). [76, Hydrocarbon processing 2011]

Driving force for implementation

Hydrotreating offers a lower operating cost.

Example plants

Many examples exist.

Reference literature

[76, Hydrocarbon processing 2011], [207, TWG 2001], [231, Sequeira 1998].

4.3.5 Storage and benchmarking of solvents

Storage and benchmarking techniques are part of the VOC abatement programme (see Section 4.23.6.1).

4.3.6 Sulphur treatment from hydrogenation units

Description

Hydrogenation processes generate H₂S. As a consequence, off-gases containing H₂S are recovered in a sulphur recovery plant (see Section 4.23.5) or are incinerated. This will become more relevant over time since new lube oil units will be increasingly based on hydrogenation processes.

Achieved environmental benefits

Reduction of sulphur and H₂S emissions.

Cross-media effects

Amine recovery of H₂S consumes energy and chemicals. Sulphur recovery units consume energy (see Section 4.23.5). Incineration requires fuel.

Operational data

See Section 4.23.5.

Applicability

In stand-alone lube oil refineries, the small amounts of H₂S generated in this process are typically incinerated. Sulphur recovery is less commonly applied in these specialised refineries.

Economics

For more information on economics, see Section 4.23.5. Data from EU refineries have shown that the implementation of SRU in stand-alone lubricant refineries producing more than two tonnes of sulphur per day is cost-effective.

Driving force for implementation

Reduction of sulphur oxide and H₂S emissions.

Example plants

At least one specialised European refinery has a SRU which recovers 99.1 % of the sulphur in the acid gas.

Reference literature

[174, HMIP UK 1995], [207, TWG 2001].

4.3.7 Stripping of waste water from aromatic extraction

Stripping techniques applicable to aromatic extraction waste water are addressed in Section 4.24.

4.3.8 Energy use and integration

Description

A group of energy-saving activities can be applied to the design, operation and maintenance of the base oil production units (see also Section 4.15 for the entire refinery integrated approach).

Design: Selecting hydrogenation-based processes normally leads to lower energy usage than solvent-based ones. A conventional solvent-based base oil lube complex is energy-intensive. The main reasons are:

- the high amount of heat required to evaporate the solvents and to recover them from the raffinate and extract streams;
- the heat needed for keeping the product streams in the liquid state;
- the deep-freezing conditions for dewaxing/de-oiling of base oil streams.

Combining aromatic extraction with hydrofinishing may lead to lower energy usage.

Operational: Use of advance process control or pinch analysis aims at achieving heat integration within the unit itself and with other units in the refinery (see Section 4.15).

Retrofitting existing process units that usually have individual energy sources (e.g. furnaces or boilers) with a common hot oil system coming from a single source may be used for heat transfer to all the solvent recovery units. When the base oil production units have a single energy system, the introduction of clean-up facilities in the flue-gases is more cost-effective. (See Section 4.23.)

Achieved environmental benefits

The reduction of SO_x, NO_x and particulate emissions to air from a single, energy-wise, optimised system compared to several individual furnaces.

Cross-media effects

See different cross-media effects for the abatement of SO_x, NO_x and particulates in Section 4.23.

Operational data

See Section 4.23 for waste gas treatments. See Section 3.3 on the operational costs of various units.

Applicability

Generally applicable to new units. This technique may nevertheless be difficult to apply to existing refineries.

Economics

See Section 4.23.

Driving force for implementation

Reduction of SO_x, NO_x, particulates emissions from the energy system. The main driving force is the energy efficiency. The heat integration within the process can be performed in a very energy- and cost-efficient way and provide stable process conditions.

Example plants

Some stand-alone lubricant refineries have already applied this concept and have switched to a common single heating source to reduce emissions coming from the burning of liquid fuels.

Reference literature

[207, TWG 2001].

4.3.9 Catalytic processes based on hydrogenation

Description

The hydrogen conversion technology converts undesired components directly to end products. The base oils are hydrofinished at higher pressure (>100 bars) than the around 30 bars pressure applied in conventional manufacturing. This technology has significantly lower operational costs but substantial initial investment. (See also Section 2.3.)

Achieved environmental benefits

No use of toxic solvents and thus no emission to air or water of these substances.
Moderate energy usage and corresponding lower emissions to air. The undesired compounds are not separated with the need for treatment or disposal but are converted into useful species.
The more recent processes normally allow a wider range of feedstock usages.

Cross-media effects

Hydrogen streams may be generated and will need further treatment.

Operational data

See Section 2.3.

Applicability

Applicable to new installations or major revamping of existing installations.
Installing hydrogenation-based units upstream of existing units is also possible to create a hybrid lube oil complex.

Economics

Lower investment and operating costs than for solvent-based processes. See Section 2.3.

Driving force for implementation

Less dependence on feedstock (more flexibility), lower investment cost, simpler process.
To produce non-carcinogenic naphthenic base oils.

Example plants

MOL refinery (HU).

Reference literature

[76, Hydrocarbon processing 2011], [137, Szeitl et al.2008], [141, TWG FI 2012].

4.3.10 Improved solvent-based plants with lower loss of containment

Description

Incorporating design and optimisation features reduces the emissions to air and water of pollutants such as toxic solvents. The solvents used in base oil production are potentially harmful and need to be contained. In order to prevent and reduce the emissions to air or water from base oil production processes, the operator can use the following techniques:

- Closed process including a solvent recovery.

- Dedicated solvent sewage routed to recovery unit: depending on the plant configuration and process waste stream generated, a separate facility may be dedicated to treat streams containing solvents. A process concentrates solvents for further recovery or reprocessing. The recovered water is routed to a central WWT or used elsewhere.
- All vents channelled to a header: Use of closed piping systems for draining and venting hydrocarbon-containing equipment prior to maintenance, particularly when containing more than 1 % w/w solvent. Ideally, permanent piping can be used to minimise the risk of exposure during the breaking of containment.
- Closed-loop sample systems routing the sampling flow back to the process.
- Canned pumps or magnetically driven pumps whenever feasible for services processing high solvent content streams. Otherwise use pumps fitted with double mechanical seals.
- Include the relevant units in a LDAR programme to minimise fugitive emissions and ensure and repair of flanges/valves etc. (see Section 4.23.6.1).
- Use high-integrity packing materials in manual or control valves with rising stems.

Achieved environmental benefits

Lower emissions to water and to air of hazardous substances such as toxic solvents.

Cross-media effects

Higher energy consumption of some of the end-of-pipe abatement techniques applied.

Operational data

See Chapter 2.3.

Applicability

Applicable to new installations and existing installations that might undergo a major retrofit.

Economics

No data available.

Driving force for implementation

Economic benefits on reducing solvent usage by higher degree of containment and recovery.

Example plants

No information.

Reference literature

[138, Hsu et al.2006]

4.4 Bitumen production

4.4.1 Storage of bitumen products

Description

Bitumen should be stored in proper storage tanks normally under heating conditions and insulated. Bitumen is generally not handled as a solid. Loading and unloading of the tank is typically done as follows: when the tank is filled, nitrogen does not flow to the tank, and the pressure is lowered by letting part of the gas go to the atmosphere; when the tank is unloaded at a low speed, a small amount of nitrogen is led to the tank; however, when the speed of unloading is higher, higher amounts of nitrogen must be used. If the tank is equipped with a cleaning system, it is mechanically very simple and easy to clean. More information on storage is available in Section 4.21.

Achieved environmental benefits

For preventing fire due to autoignition of condensed vapours, tanks containing oxidised bitumen are equipped with nitrogen blanketing and pressure/vacuum safety valves. These valves need maintenance due to the slime. In some cases, these valves may be removed and a gaseous overhead treatment scheme is used. As an example, see the new unit (2010) in CEPSA Huelva (Spain).

Cross-media effects

Hydrocarbons and sulphur compounds may emanate from leakages (particularly in overhead systems) and pressure relief valves and in the form of liquid droplet-containing aerosols from the venting of tanker top-loading operations.

Operational data

Electricity, hot oil and low-pressure steam can be used for heating. The heat exchanger can be inside the tank or outside the tank, in which case bitumen is circulated through it. Differences in temperature should not be too high due to the surface temperature and coking.

Applicability

Bitumen products are stored in refineries that have bitumen production. Prevention techniques, as mentioned, are typically applied.

Economics

None available.

Driving force for implementation

For safety, i.e. to prevent accidents, bitumen tanks are equipped with nitrogen blanketing and a pressure/vacuum safety valve.

Example plants

Some refineries in Europe use the techniques mentioned here. There is a recent unit (2010) in Huelva (Spain).

Reference literature

[207, TWG 2001].

4.4.2 Techniques to control emissions to the air

4.4.2.1 Treatment of the gaseous overheads

Description

Oxidiser overheads can be routed to a scrubber rather than direct water quenching for contaminant removal prior to incineration. The off-gases are condensed in a scrubber, where most of the hydrocarbons are eliminated. The water vapour (sometimes after full condensation) is left in the air stream to incineration at a temperature of approximately 800 °C.

Achieved environmental benefits

Reduction of H₂S, SO₂, SO₃, CO, VOC, particulates, smoke and odour emissions.

Cross-media effects

Additional contaminated water. Scrubber water is dirty and requires oil and solids separation prior to reuse as desalted wash water and/or biotreatment. The sour water from the scrubber is routed to a sour water stripper and stripped prior to reuse and/or purification.

Applicability

Typically applied to overheads from the bitumen blowing systems.

Example plants

Many plants in Europe, e.g. the recent unit (Biturox design - 2010) in CEPSA Huelva (Spain), use a gaseous overhead treatment scheme.

Reference literature

[174, HMIP UK 1995].

4.4.2.2 Use of the heat from incondensable products and condensates

Description

Both incondensable products and condensates from the separator, hydrocarbon and aqueous unit can be burnt in a purpose-designed incinerator, using support fuel as necessary or in process heaters.

Oxidiser overhead slop oil can also be treated in the sludge processing or recycled in the refinery slop oil system.

Achieved environmental benefits

Reduction of emulsion of light oil, water and particulates. Another environmental benefit is the removal of odorous incondensables which are difficult to treat elsewhere.

Cross-media effects

On scrubbing, aerosols can give rise to plugging. Water streams can become contaminated. In a well-operated unit, SO₂ or odour from the incineration of bitumen-blowing incondensables do not pose any problem.

Operational data

The incinerator should operate at a temperature of at least 800 °C and the combustion chambers should have a residence time of at least 0.5 seconds. The oxygen concentration at the combustion chamber outlet should be greater than 3 % v/v. Low-NO_x burners can be fitted in these incinerators.

Applicability

Widely used to get rid of bitumen fumes. Incondensables and/or condensates can be burnt in process heaters. However, they should be treated or scrubbed to remove compounds of sulphur or combustion products that may cause odours or other environmental problems.

Driving force for implementation

Reduction of odours, sludge and oily waste.

Example plants

Many bitumen oxidisers have associated facilities to handle gas and liquid wastes.

Reference literature

[174, HMIP UK 1995]

4.4.2.3 Treatment of vents from the storage and handling of bitumen materials

Description

Techniques that may be applied to prevent VOC emissions and odours include:

- venting of odorous gases during the storage of bitumen and the venting of tank blending/filling operations to an incinerator;
- the use of compact wet electrostatic precipitators which have been proven capable of successfully removing the liquid element of the aerosol generated during the top-loading of tankers;
- adsorption on activated carbon.

Achieved environmental benefits

Reduction of emissions of sulphur compounds, VOC, particulates, smoke and odour emissions.

Cross-media effects

Energy consumption and, in the case of a wet ESP, waste generation.

Operational data

In the waste gas of a cleaning unit, a mass concentration of VOCs of a total of 150 mg/Nm³ can be complied with. In the waste gas of an incineration plant, a mass concentration of VOCs, given as total C, of a total of 20 mg/Nm³ can be complied with (half-hourly mean values attainable in operations).

Applicability

Fully applicable.

Driving force for implementation

Reduction of emissions and nuisances.

Reference literature

[167, VDI 2000], [174, HMIP UK 1995].

4.4.2.4 Sulphur dioxide abatement and sulphur recovery units

Description

SO_x abatement techniques and sulphur recovery units (SRU) are techniques to reduce sulphur emissions. They are extensively documented in Section 4.23.

4.4.3 Waste water pretreatment techniques

Description

Oxidiser overhead waste water accumulated in the overhead condensate collection drum can be sent to a sour water stripper prior to sending it to the effluent water treatment facilities. In some particular schemes, water from the oxidiser is not suitable for the SWS and is sent directly to the WWTP. More information on waste water treatment is available in Section 4.24.

Achieved environmental benefits

The stripping reduces the H₂S, oil, aromatics, volatile PAH, sulphuric acid and odorous oxidation products (ketones, aldehydes, fatty acids) in the sour waste water, reducing the charge to the central waste water system of the refinery.

Cross-media effects

An increase in oil and particulates load to the sour water stripper.

Operational data

None available.

Applicability

Typically applied to waste water from bitumen blowing.

Economics

None available.

Driving force for implementation

Reduction of the pollutant charge to the refinery waste water.

Reference literature

[174, HMIP UK 1995], [207, TWG 2001].

4.4.4 Hot oil system

Description

When the bitumen production units have a single energy system, the introduction of clean-up facilities for the flue-gases is more cost-effective. More information is available in Sections 4.23 and 4.3.8.

Hot oil systems using oil as a medium by heating coils are used for maintaining bitumen fluid during storage.

4.5 Catalytic cracking

4.5.1 Hydrotreatment of feed to the catalytic cracker

Description

Hydrotreatment of feed to the catalytic cracker operates at similar conditions as those for fuel oil and atmospheric residue hydrotreatment (see Sections 2.13 and 4.13). In a growing number of refineries, a hydrotreating or hydrocracking unit is added upstream of the FCC unit, mainly for the purpose of producing low-sulphur gasoline and diesel (<10 ppm) and for optimising the process configuration towards the maximisation of heavy residue conversion and middle distillate production. Simultaneously, this additional treatment also benefits the reduction of FCC emissions, leading to a substantial abatement of SO₂. There are also effects on NO_x but they will be driven more by regenerator temperature and combustion dynamics.

Achieved environmental benefits

FCC feedstock hydrotreatment can reduce the sulphur content to <0.1 – 0.5 % w/w (depending on the feedstock). Given that around 9 % of this sulphur content is normally emitted in the regenerator flue-gas, emissions of SO₂ from the regenerator can be reduced by up to 90 % as a consequence of the hydrotreatment. The resulting flue-gas daily average concentration can remain in the range of 25 – 600 mg/Nm³ (3 % O₂) depending on the feedstock. One refinery reported values over 600 mg/Nm³ associated with fluctuations of sulphur content around 0.5 %. It is reported that the yearly average concentration can be decreased to as low as 89 mg/Nm³ (3 % O₂) [54, Gallauner et al. 2009].

Nitrogen compounds can also be reduced by up to 75 – 85 % (smaller percentage for the partial combustion mode), although a certain reduction of nitrogen compounds does not lead to an equivalent NO_x reduction (when it occurs, a maximum NO_x reduction of approximately 50 – 60 % is achieved from a 70 – 80 % nitrogen reduction in the feedstock). The resulting flue-gas daily average concentration can remain in the range of 50 – 180 mg/Nm³ (3 % O₂) depending on the feedstock, with a yearly average concentration as low as 71 mg/Nm³ (3 % O₂) [54, Gallauner et al.2009].

This process also reduces the metal emissions (e.g. Ni, V) to the air and prolongs the life of the catalytic cracker catalyst.

Another benefit of this technique is a lower concentration of mercaptans in the products. This may impact the next process stage which is the mercaptan removal. This reduces the amount of used caustic and emissions into water.

Cross-media effects

Cross-media effects include the increase of energy consumption and the consequent increase in CO₂ emissions, due mainly to the hydrogen, as discussed in Section 3.14. As an example, the overall energy consumption of a refinery increased from approximately 2 to 2.5 GJ/tonne refined after the addition of a hydrocracker (3 Mt/yr) and a complementary steam methane reforming H₂ production plant (220 000 t/yr).

Nevertheless, as hydrotreatment is generally required for products specification compliance, assessing the corresponding cross-media effects requires taking into account those that already exist.

As discussed in Section 4.13, hydrotreatment processes generate catalysts for disposal and increase the H₂S production, with direct consequences for the sour water stripper and sulphur recovery units (which may need to be enlarged or replaced). In addition, heavy metals in FCC feedstock will be shifted from the FCC to the hydrotreater catalyst. Deep hydrotreatment, by reducing the metal content, may also lead to a reduced performance of the ESP (see Section 4.5.5.2).

Operational data

The sulphur removal efficiency achieved by hydrotreatment depends on the boiling range of the catalytic cracker feed. The heavier the feed, the more energy is required for the same sulphur removal efficiency. The water used for the different catalytic sections yields 20 – 40 m³/h of sour water.

The proportion of catalytic cracker feed that is hydrotreated varies by quite a lot depending on the refinery configuration and strategy. The several sources of feed include:

- vacuum gas oil fraction 375 – 560 °C (main source),
- atmospheric distillation fraction (>375 °C),
- other streams including imported streams.

Data on the effect of the feedstock hydrotreatment on the cracker's PM emissions have also been provided in Table 3.38.

The following graphs (Figure 4.1 and Figure 4.2 below) show the performance obtained after the commissioning, in mid-2005, of a new 1 Mt/yr hydrocracking unit upstream of a 1.5 Mt/yr FCC unit in a European refinery. The average emission from the FCC unit fell from a yearly average of 1 650 to 670 t/yr (-60 %) while the corresponding average sulphur content in its feedstock decreased from 1.5 – 1.7 % to 0.25 – 0.35 %. For this particular application, the related specific consumption of hydrogen is in the range of 8 – 9 kg H₂ per tonne of hydrotreated feedstock.

Applicability

Fully applicable. This process is more cost-effective when sufficient hydrogen, SWS and SRU capacities are already available in the refinery. The main driving force for the application of this technique is nevertheless the optimisation of the refinery configuration.

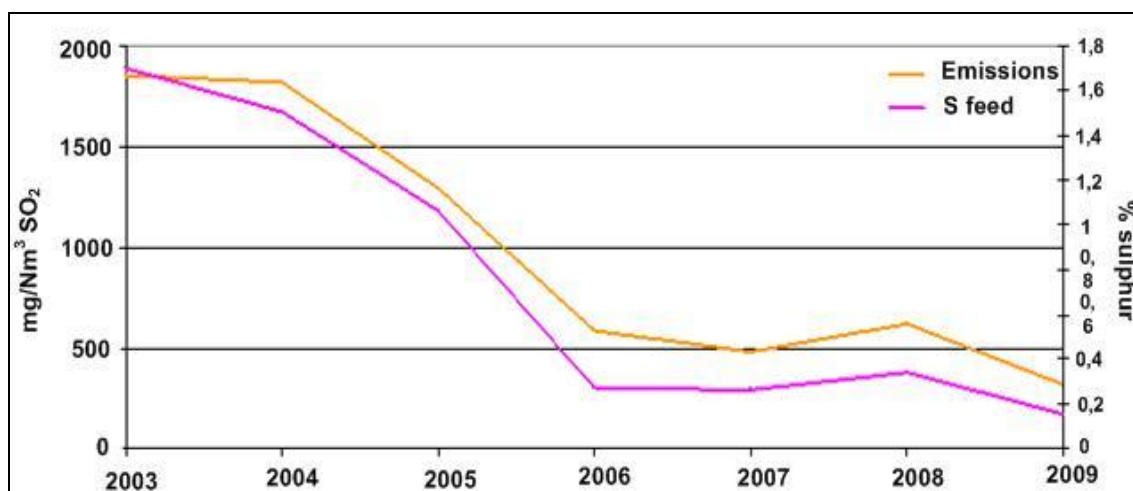


Figure 4.1: Evolution of the feed S content and SO₂ emissions after FCC feed hydrotreatment

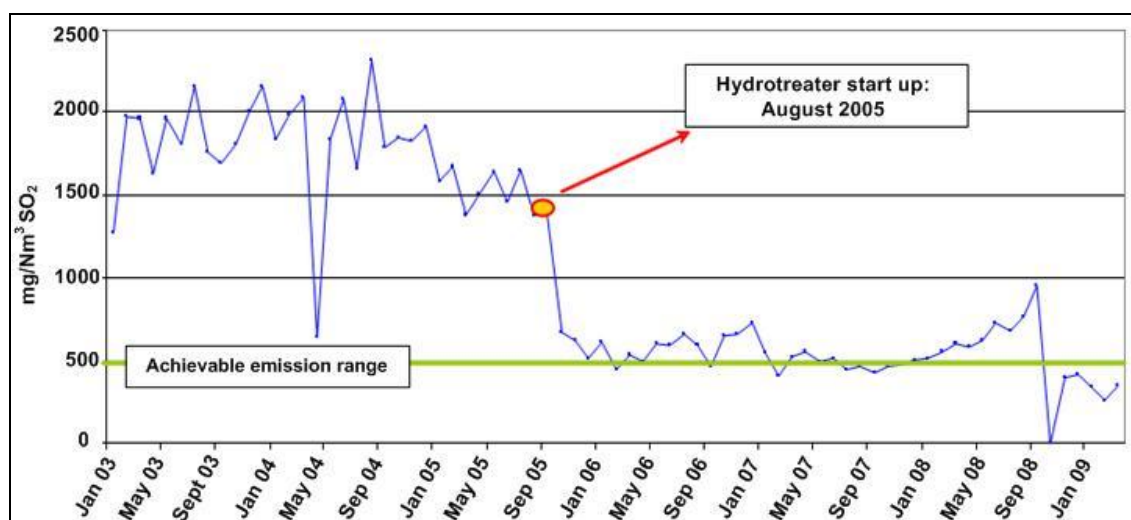


Figure 4.2: Monthly average SO₂ emissions after FCC feed hydrotreatment

Economics

Table 4.10 and Table 4.11 give examples of costs associated with FCC feedstock hydrotreatment.

Table 4.10: Catalytic feed hydrotreatment (typical feeds being atmospheric residue and vacuum gas oil)

| Size/capacity (ktonnes/yr) | Typical capital/installed cost (EUR million) costs include necessary interconnections to existing plant for integration purposes | Operating cost (EUR million/yr) |
|----------------------------|---|---------------------------------|
| 1 250 | 198 | 9 |
| 2 500 | 303 | 17 |
| 3 750 | 394 | 26 |

NB: The cost assumes that there is adequate space and an existing SRU (sulphur recovery unit) and sour water stripping capacity. If further hydrogen production is needed, a new hydrogen plant for a 2 500 kt/yr FCC unit feed hydrotreater or hydrocracker would typically cost in the range of EUR 60 – 75 million. Costs updated by CONCAWE, 2010

Sources: [163, FWE 1999], CONCAWE 2010

Table 4.11: Cost ranges associated with the hydrotreatment of a 1.5 Mt/yr FCC unit according to some typical configurations

| Cost parameters | Distillate feed desulphurisation | Residue feed desulphurisation | Feedstock hydrotreating to reduce NO _x |
|-------------------------------------|---|--|---|
| Capacity of process | 1.5 Mt/yr | 1.5 Mt/yr | 1.5 Mt/yr FCC unit with CO boiler |
| Investment expenses (EUR million) | 80 – 100 ⁽³⁾ 45 – 50 ^(1,2) | 200 – 300 ^(2,3) | 80 – 100 |
| Operating expenses (EUR million/yr) | 4 – 9 | 15 – 25 ⁽³⁾ 30 – 50 ² | 4 – 9 |

(¹) Excluding H₂ production and H₂S handling facilities.
(²) [151, Sema, Sofres 1991]
(³) [166, CONCAWE 1999].

A recent example (questionnaire 36) of the hydrotreating of 56 % of a 1.5 Mt/yr FCC unit feedstock gives the following costs:

- total investment (2005): EUR 230 million, including the three treatment units (cumulated capacity of 1.05 Mt/yr), the necessary adaptation of the FCC, and the related SRU and acid water treatment plant;
- energy costs: EUR 7.15/t of treated feedstock (2009);
- approximate hydrogen costs (annual): EUR 0.5 million (fixed term) + EUR 1 420/t of hydrogen supplied (2009), with a specific consumption of 8 – 9 kg H₂/t of treated feedstock;
- the total operating cost (including H₂ fixed term) is EUR 7.75/t of treated feedstock, and the corresponding specific cost is 6 640 EUR/t of SO₂ avoided.

In another example (questionnaire 32), the following data are provided for the hydrotreatment of a 3 Mt FCC feedstock:

- SO₂ emissions reduced by 3.7 kg/t of treated feedstock;
- related consumption levels are 9.6 kg of H₂, 30.8 kWh of electricity, and 556 MJ of fuels per tonne of treated feedstock;
- the total operating cost is estimated to be EUR 19.3 per tonne of treated feedstock, and the corresponding specific cost is 5 200 EUR/t of SO₂ avoided.

Note: the operating costs of hydrotreatment should also be partly affected by the improvement of the product characteristics as ultimately this is its main objective.

Driving force for implementation

The implementation of this technique is typically product specification-driven because higher conversions are achieved with hydrotreated feedstocks. The majority of the products produced by the catalytic cracker without previous hydrotreatment need further treatment to comply with product specifications. Moreover, the flue-gas from the regenerator contributes significantly to the overall refinery SO_x/NO_x emissions. Desulphurisation or mild hydrocracking of the feed is an option to reduce these emissions.

Example plants

Many examples: 16 out of the 56 European sites reported by TWG members were said to use this technique.

Reference literature

[220, IFP 2000], [166, CONCAWE 1999], [163, FWE 1999], [151, Sema, Sofres 1991], [191, UBA Austria 1998], [221, Italy 2000], [207, TWG 2001], [Specific attachments to Questionnaires n° 31, 32, 36, 39], [270, CONCAWE 2012].

4.5.2 Waste heat boiler and expander applied to the flue-gas from the FCC regenerator

Description

Heat recovery from the regenerator flue-gas is conducted in a waste heat boiler or in a CO boiler. Heat recovery from the reactor vapour is conducted in the main fractionator by heat integration with the unsaturated gas plant, as well as by feed preheating and by the generation of steam with the residual heat from product run down streams and pump-around streams. The steam produced in the CO boiler normally balances the steam consumed in the FCC. Installing an expander in the flue-gas stream from the regenerator can further increase energy efficiency. Figure 4.3 gives a simplified scheme of the application of a waste heat boiler.

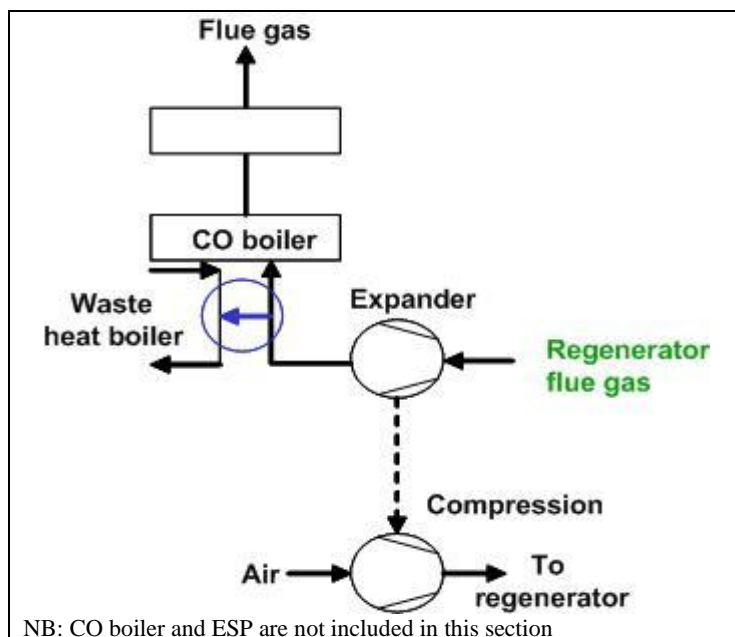


Figure 4.3: Waste heat boiler and expander applied to the regenerator flue-gas of a catalytic cracker

Achieved environmental benefits

The waste heat boiler recovers the heat from the flue-gas and the expander recovers part of the pressure for use in the compression of the air needed in the regenerator. An example of the application of an expander saved 15 MW_e from the flue-gas generated by a FCC with a capacity of 5 Mt/yr.

Cross-media effects

Significant quantities of catalyst fines are collected in the waste heat boiler (WHB). The newer WHBs avoid catalyst arrival by using configurations which include e.g. cyclones or have facilities which permanently remove the collected fines (e.g. sonic soot cleaners), but older WHBs are normally soot-blown once per shift. During heating-surface cleaning (or soot blowing) in CO boilers, emissions of PM and metal can increase by about 50 %.

Examples of three German refineries where ESPs are installed downstream of the FCC are shown in Table 4.12.

Table 4.12: Examples of soot blowing effects for three German refineries

| Reference | Capacity | Feed | Mode | PM | | Metals ⁽²⁾ ⁽³⁾ | |
|------------|----------|--|---------------------|--|----------------|--|---------------|
| | | | | Conc ⁽¹⁾ (mg/Nm ³) | Flux (kg/h) | Conc ⁽¹⁾ (mg/Nm ³) | Flux (g/h) |
| Refinery 1 | 82 % | Atmospheric residue, unconverted gas oil | Normal | 11.7 | 1.07 | 0.091 | 8.4 |
| | | | <i>Soot blowing</i> | 18.7 | 1.71 | 0.140 | 12.9 |
| Refinery 2 | 79 % | Atmospheric residue, heavy and light waxes | Normal | 6.70 | 0.53 | 0.076 | 6.1 |
| | | | <i>Soot blowing</i> | 10.2 | 0.80 | 0.115 | 9.0 |
| Refinery 3 | 79 % | NA | Normal | 6.70 | 0.95 | 0.033 | 3.5 |
| | | | <i>Soot blowing</i> | 9.70 | 1.43 | 0.052 | 7.7 |

⁽¹⁾ Concentrations are mean values (3*30 minutes) in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.
⁽²⁾ Metals include Ni except for Refinery 1 where they include Ni, Cu, V.
⁽³⁾ Metals determined from PM constituents deposited on quartz filters according to national requirements.
Source: TWG 2010

Operational data

Energy recovery from the regeneration gas reduces the CO boiler duty, but contributes to an overall higher energy recovery from the FCC.

Applicability

Retrofitting of this equipment can be very difficult because of space limitations in the refinery. For small or low-pressure units, expanders are not justified economically.

Economics

Applying an expander on the regenerator gas could be costly because of the additional high-temperature particulate systems required. Turbo expanders are costly items and so are waste heat recovery units.

Driving force for implementation

Recovery of energy.

Example plant(s)

Energy recovery by utilising an expander in the regenerator flue-gas is only applied in the larger, more recently built units.

Reference literature

[172, MRI 1997], [207, TWG 2001], [263, TWG 2010].

4.5.3 Catalyst selection

Description

Techniques to consider include:

- Use of a higher quality FCC catalyst. Process efficiency and metal tolerance (to V and Ni in particular) can be increased, while catalyst waste can be reduced and the rate of replacement reduced.
- Use of an attrition-resistant catalyst to reduce the amount of catalyst added on a daily basis and to reduce the emission of particulates from the regenerator. Emissions reductions result from both a decrease in the small particulate emissions from the fresh catalyst, as well as from the catalyst resisting attrition during unit operations. These catalysts are typically alumina-based (e.g. the Al-sol binder technology) and particulates arising from their use are much harder than from the silica-based former catalyst generation.

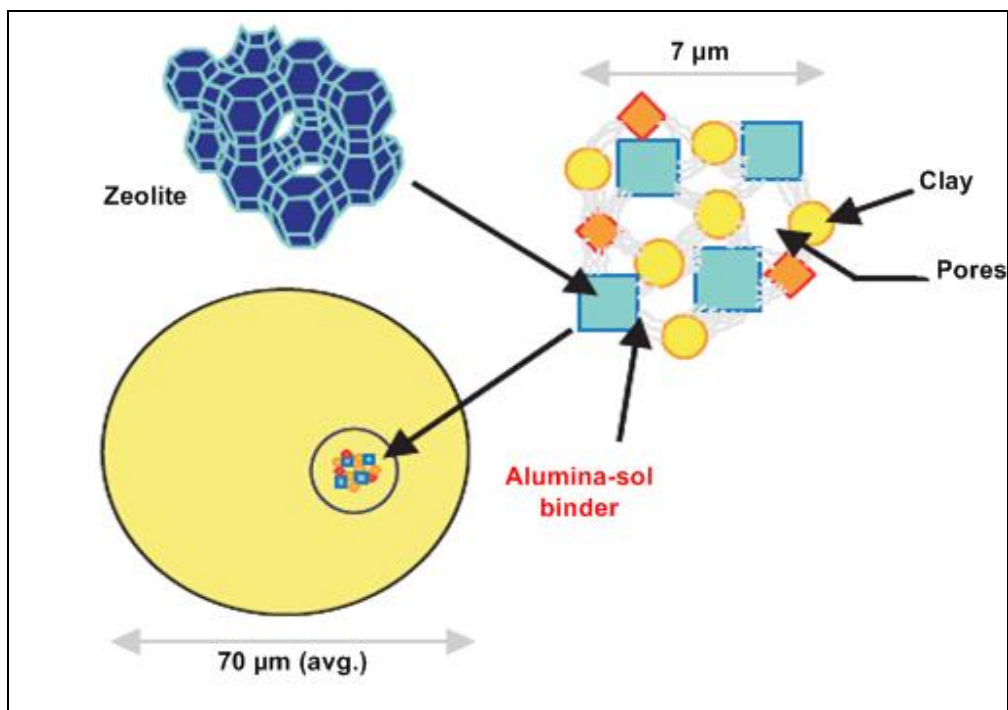


Figure 4.4: Typical structure of a low attrition catalyst for the FCC process

Achieved environmental benefits

A good selection of the catalyst used in the FCC process can:

- increase the FCC efficiency by up to 20 %, coke production can be decreased and catalyst waste can be reduced;
- increase the recyclability of the catalyst;
- reduce the particulate content of flue-gas before treatment to 300 mg/Nm³.

Cross-media effects

None in particular.

Operational data

Based on data available from a 100-day trial [24, Bruhin et al.2003], switching from a Si-sol catalyst to an Al-sol catalyst can reduce PM emissions (considered at constant % O₂) by up to 50 % after a transitory period of 50 – 100 days.

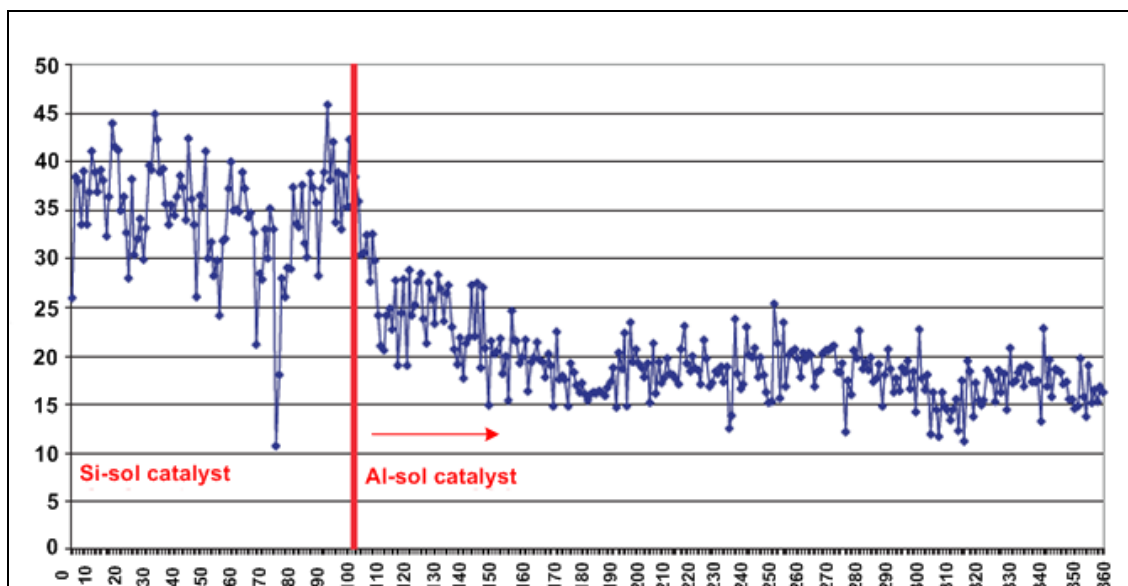


Figure 4.5: Effect of a low attrition catalyst on PM emissions (mg/Nm^3) after 100 days

Applicability

If not yet optimised, a change in the catalyst is usually favoured. In exceptional cases, however, it may have an adverse effect on the performance on the FCC.

Economics

Investment expenses: none.

Operating expenses: negligible.

Driving force for implementation

Process requirements and reduction of finest size PM emissions.

Example plants

Most FCC units in Europe have already optimised catalyst selection.

Reference literature

[24, Bruhin et al.2003], [156, MCG 1991], [166, CONCAWE 1999].

4.5.4 Nitrogen oxides abatement techniques

This section includes NO_x abatement techniques that may be applied to FCCs. Among these are process-related techniques, which are very specific and mostly involve the reduction of NO_x by using or improving various catalysts and additives and by acting on the three major sources of nitrogen in the FCC regenerator: nitrogen compounds in the coke resulting from the feed, nitrogen from air admitted in the regenerator, and nitrogen from the combustion air to CO boilers in the case of partial-burn units. A strong relationship is observed between NO_x and excess O_2 in the flue-gas, and a poor distribution of O_2 in the regenerator bed can result in large variations of local scale NO_x formation.

4.5.4.1 Selective catalytic reduction (SCR)

Description

See Section 4.23.3.3.

Achieved environmental benefits

For FCC application, inlet NO_x concentrations to the SCR may vary from 200 to 2 000 mg/Nm^3 at 3 % O_2 , depending on the type of FCC used (total or partial combustion in combination with a CO boiler) and the type of feed used (heavier feed tends to produce higher NO_x emissions). A reduction of up to 80 – 90 % of NO_x emissions with the outlet concentration of NO_x reduced to 20 – 250 mg/Nm^3 at 3 % O_2 can be achieved, depending on the inlet concentration. As an example, such reduction efficiencies may correspond to saving approximately 300 tonnes of NO_x per year from a catalytic cracker with a capacity of 1.65 Mt/yr (calculation based on an average of 450 mg/Nm^3 inlet and 50 mg/Nm^3 outlet, with a $0.7 \cdot 10^9 \text{ Nm}^3/\text{yr}$ waste gas flow).

Most SCR systems include an upstream section with a CO oxidation catalyst that shares SCR installation and achieves up to 95 % CO conversion to CO_2 . In SCR systems not equipped with a CO oxidation catalyst, small conversions to CO_2 occur when CO reacts with NO and generates molecular nitrogen.

Cross-media effects

See Section 4.23.3.3. Concerning, more specifically, FCC units, the application of SCR may reduce the potential for energy recovery using expander turbines, as it increases the pressure drop over the regenerator overhead circuit and is also prone to a build-up of pressure drop over time, thereby limiting the available operating window for a turbine expander, particularly in existing facilities with fixed pressure profiles. This may lead to a lower thermal efficiency.

Operational data

Catalyst performance and the pressure drop of SCR operated on FCC units are expected to deteriorate over time, mainly due to fouling by PM catalyst fines and SO_x salts. The theoretical expected catalyst lifetime is about four years but could be very different, depending on the PM filtering efficiency upstream of the SCR and the operating conditions. The two following examples are very illustrative on this matter.

- Intensive fouling has been experienced and deeply analysed in one European site: as seen in Figure 4.6, this is was mainly due to an excessive inlet gas temperature (most of the time above 362 °C and sometimes above 370 °C), which drove the operator to increase the NH_3 injection rate up to 120 % of the theoretical stoichiometry, in order to compensate the poor conversion.
- In contrast, current examples in Europe have shown lifetimes well over expectations, reaching six to seven years and even much longer. In one particular case, the first three SCR catalyst layers installed at Preem Lysekil refinery (SE) in 1994 (and also the fourth one installed in 2003) were still in operation in 2010. Based on the latest tests, a lifetime of 140 000 to 150 000 hours is expected.

SCR applied below design loads and careful dedusting of the inlet gas upstream of the SCR help to increase catalyst lifetimes. Particle size distribution and particulate load of the flue-gas entering the SCR should be evaluated to determine whether there is potential for fouling (high particulate) and/or thermophoretic fouling (small particulates). If necessary, particulate mitigation equipment, such as sootblowers, may need to be installed. More general operational data for SCR can be found in Section 4.23.3.3.

Table 4.13 illustrates the results obtained for some FCC units equipped with SCR treatment.

Table 4.13: Performances reported as obtained with SCR for six FCC units

| Data-set reference [Questionnaire] | Type | Inlet | Outlet | % NO _x abatement | Ammonia slip | SCR shutdown frequency/Other information |
|---|---|----------|------------------------------|-------------------------------|----------------|--|
| CONCAWE 1 ⁽¹⁾ (²) | Full combustion with auxiliary fired boiler | 36 – 244 | 2 – 26 | 88 % | – | 4 years |
| CONCAWE 2 ⁽¹⁾ (²) | Full combustion unit | 25 – 211 | 3 – 13 | 91 % | – | 7 – 17 months |
| CONCAWE 3 ⁽¹⁾ (²) | Partial-burn with CO boiler | 318 | 99 | 85 % (<70 % at end of run) | – | 4 years |
| [n° 27] ⁽³⁾ | Full combustion unit | – | 249.6 | 79.1 % | – | – 1 351 t avoided (2006) |
| US refinery CITGO Lemont (IL) | NA | 200 ppmv | <20 ppmv (⁴) | 90 % | – | Commissioned 2008 Wet gas scrubber is in place downstream of the SCR |
| US refinery SHELL Deer Park (TX) | NA | 200 ppmv | <20 ppmv (⁴) | 90 % | Not measurable | Commissioned 2004 Flue-gas desulphurisation is in place downstream of the SCR |

(¹) Daily average in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.
(²) Averages are calculated from the 5th – 95th percentile range of the complete available data-set.
(³) Yearly averages in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.
(⁴) 365-day average based on the continuous emission monitoring system expressed as ppmv at 0 % O₂; 20 ppmv NO_x is around 32 mg/Nm³ at 3 % O₂.
Sources: 1 – 3: CONCAWE; 27: TWG 2010 data collection; US refineries: [140, Jensen-Holm et al.2010.]

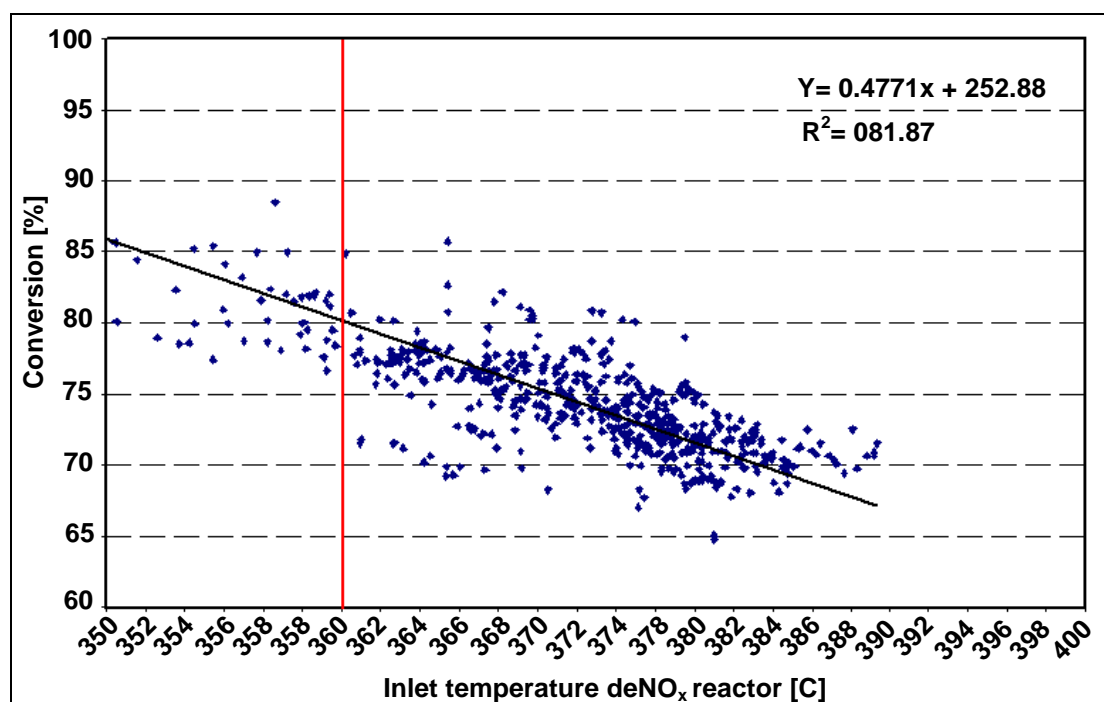


Figure 4.6: SCR conversion yield as a function of inlet temperature for a European FCC unit

Applicability

Because the temperature window is wide (300 – 400 °C), SCR is relatively flexible for FCC retrofit applications. However, existing auxiliary fired boilers, CO boilers and waste heat boilers may have to be modified for temperature adjustment.

Considerable space is needed for the installation. SCR applications often require a new waste heat boiler (full burn) or a CO boiler (partial burn) if they are not present. Preferably the NO_x reduction unit is integrated into the waste heat boiler. Because SCR operates at oxidising conditions, it cannot be installed upstream of a CO boiler (partial burn).

As the SCR catalyst could potentially be fouled by the particulates present in the flue-gas stream, additional filtering might be required upstream of the new SCR unit.

As for an SNCR, the ammonia dosing rate is limited by the potential risk of corrosion downstream of the unit.

Economics

Table 4.14 shows some examples of the economics of the application of SCR to FCCs.

Table 4.14: Economics of SCR applied to FCC units

| Size of the FCC (Mt/yr) | Efficiency (%) | Outlet NO _x concentration (mg/Nm ³) | Installation cost (EUR million) | Operating and maintenance cost (EUR million/yr) | Specific removal cost ⁽⁴⁾ (EUR/t of NO _x removed) |
|-------------------------|----------------|--|--|---|---|
| 1.65 | 90 | 40 | 3.8 (SEK 33 million) ⁽¹⁾ ⁽²⁾ | 0.24 (SEK 2 million) ⁽³⁾ | 2 103 |
| 1.5 | 85 | 120 | 6.3 – 13 | 0.4 – 0.8 | 2 023 |
| 1.5 | 85 | 37.5 | 1.2 – 3.6 ⁽⁵⁾ | 0.12 – 0.48 | 2 042 |

⁽¹⁾ Cost in original currency – Built 1994.
⁽²⁾ Including a SCR reactor, ammonia storage and injection facilities and initial fill of catalyst.
⁽³⁾ Operation and maintenance cost including ammonia, steam and replacement of catalyst.
⁽⁴⁾ Including a CO boiler.
⁽⁵⁾ Using the same economic analysis presented in Table 4.15.
 NB: All costs for a new SCR installation.

In addition, recent cost data for using SCR and SNCR are shown in Table 4.17.

A more detailed economic assessment of SCR in a FCC unit (year 2000) is shown in Table 4.15.

Table 4.15: Main cost factors for a selective catalytic reduction (SCR) installation (raw gas) after the FCC plant

| Cost parameters | Quantity | EUR/unit | EUR/yr |
|--|----------|---------------------------|----------------|
| Operating hours (h/yr) | 8 000 | | |
| Investment costs (EUR million) | 1.45 | | |
| Input factors for annual expenditure: Number of years Rate of interest (%) | 15 6 | | |
| Annual repayment incl. interest (EUR/yr) | 150 000 | | |
| Proportional investment costs incl. interest | | | 150 000 |
| Volume of catalyst (m ³) | 20 | | |
| Duration (years) | 8 | | |
| Renewal of catalyst (m ³ /yr) | 2.5 | EUR 15 000/m ³ | |
| Average renewal of catalyst (EUR/yr) | 36 300 | | |
| Catalysts | | | 36 300 |
| Maintenance + wear and tear (% of investment costs) | 2 | | |
| Maintenance + wear and tear (EUR/yr) | 29 000 | | |
| Maintenance + wear and tear | | | 29 000 |
| Pressure drop (mbar) | 8 | | |
| Energy for reheating (MJ/h) | 0 | EUR 3.6/GJ | 0 |
| Electrical energy (kWh/h) | 88 | EUR 0.065/kWh | 46 000 |
| NH ₃ liquid (kg/h) | 36.96 | EUR 0.25/kg | 75 200 |
| Total costs | | | 336 269 |
| NB: In a refinery with a volume of exhaust gas of 100 000 Nm ³ /h achieving a NO _x emission reduction of 1 000 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <200 mg NO _x /Nm ³ . The inlet concentration may vary between 200 and 2 000 mg/Nm ³ at 3 % O ₂ . The outlet concentration of NO _x is reduced to 80 – 120 mg/Nm ³ by SCR. | | | |

See also Table 4.18 for a cost comparison of various techniques.

Based on the CONCAWE 6/11 report, the costs (2011) for a 2Mt/yr unit are estimated as follows (see Annex 8.3):

- capital costs: EUR 50 – 75 million,
- annual cost: EUR 6 – 14 million,
- cost per avoided tonne of pollutant: EUR 25 000 – 60 000/t NO_x.

A preliminary evaluation for the retrofitting of a 57 500 bpd (3Mt/yr) FCC with SCR gives the following figures (2007):

- capital cost: GBP 15 million (EUR 22.2 million on 2/07/2007),
- operating cost: GBP 0.54 million per year (EUR 0.80 million per year),
- estimated quantity of NO_x abated: 80 t/yr (assumed reduction yield of 50 %),
- equivalent annual cost: GBP 34 079 (EUR 50 442) per t/yr of NO_x abated (15-year lifetime assumed).

Driving force for implementation

Reduction of NO_x emissions.

Example plants

At least six SCR units are in operation in FCCs worldwide and two in Europe: Preemraff Lysekil (Sweden) and Shell in Pernis (Netherlands).

Reference literature

[17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009], [139, CONCAWE 6/11 2011], [151, Sema, Sofres 1991], [160, Janson 1999], [166, CONCAWE 1999], [172, MRI 1997], [191, UBA Austria 1998], [198, UKPIA 2000], [228, TWG 2000], [246, AL Group 2001], [Site questionnaires n°27, 39, 42].

4.5.4.2 Selective non-catalytic reduction (SNCR)**Description**

See Section 4.23.3.2 for a general description of the SNCR technique.

Achieved environmental benefits

On FCC units, this technique achieves NO_x reduction levels from 30 % to 50 % and has shown to be able to achieve NO_x reductions of up to 70 % (on a daily basis). The outlet concentrations can be as low as <100 – 200 mg/Nm³ at 3 % O₂ depending on the nitrogen content of the feedstock.

Cross-media effects

See Section 4.23.3.2 for a description of the general cross-media effects of SNCR.

One issue of particular concern with SNCR applications to FCC units is the potential increase in CO emissions. At the lower end of the SNCR operating temperature range, ammonia can inhibit CO oxidation and increase CO emissions from low-temperature CO boilers.

Operational data

Table 4.16 illustrates the results obtained for three FCC units equipped with a SNCR treatment.

Table 4.16: Performances reported as obtained with SNCR for three FCC units

| Data-set reference | Type | Inlet | Outlet | % NO _x abatement | Ammonia slip | Comments |
|--------------------|---|-----------|----------|-----------------------------|--------------|-------------------------------------|
| CONCAWE 4 | Full combustion with auxiliary fired boiler | 123 – 410 | NA | 23 | <15 | – |
| CONCAWE 5 | Full combustion with auxiliary fired boiler | 90 – 530 | 50 – 180 | 50 | 8 | 95th Perc. abatement: 81 % (hourly) |
| CONCAWE 6 | Partial combustion with CO boiler | 318 | 99 | 67 | 10 | 95th Perc. abatement: 78 % (hourly) |

NB: Daily average emissions in mg/Nm³ at 3 % O₂ (dry gas).
 Data based on continuous emission monitoring system.
 It is reported that % NO_x abatement is dependent on the inlet concentration.
 Source: CONCAWE 4/09

In a German refinery, the following data on a long time span are reported about SNCR installed on a FCC unit:

- outlet NO_x concentration: <100 mg/Nm³ (online measurements);
- outlet CO concentration: <90 mg/Nm³;
- FCC unit with CO boiler in partial combustion;
- total nitrogen content of the FCC feed: about 1 200 ppm (determined by periodic feed analyses);
- ammonium flow: 300 l/h (8 – 10 % concentration).

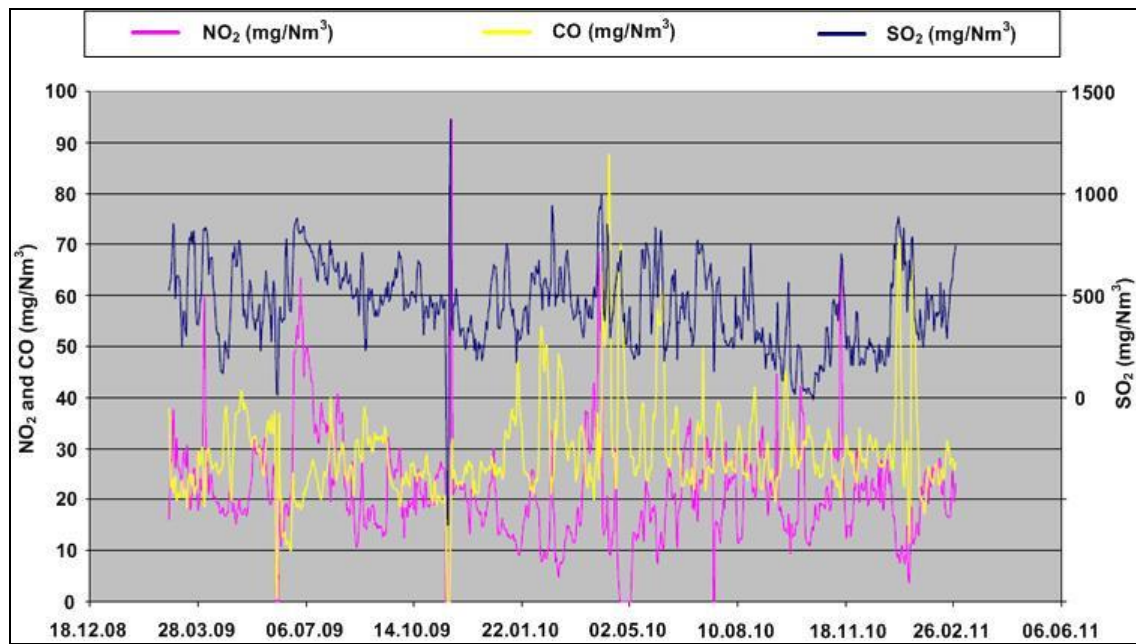


Figure 4.7: Emissions to air from a FCC unit with SNCR at a German refinery

Applicability

SNCR is applicable in partial combustion FCCs with CO boilers, and full combustion FCCs with auxiliary fired boilers, dependent on sufficient residence time in the boiler at the required temperature range. SNCR units cannot work properly during boiler shutdowns.

SNCR is also applicable to full combustion FCCs without auxiliary boilers, using hydrogen addition for injection into the regenerator overhead line. In this case, the application should take into account the unit specificity, including the starting process conditions.

Economics

Cost data for SCR and SNCR are presented in Table 4.17

Table 4.17: Economics of SCR and SNCR at FCC units – Cost-effectiveness data from a sample of 6 FCC units

| | | | | | Selective Non-Catalytic Reduction (SNCR) | | | | | Selective Catalytic Reduction (SCR) | | | | | |
|---|-------------|-------------|-------------|------------------------|--|-------------------------------------|--------------------------------|-------------------------------|----------------------------------|-------------------------------------|-------------------------------------|--------------------------------|------------------------------|---------------------------------|---|
| | | | | | Efficiency | ACC | Fixed OP | | Variable OP | Efficiency | ACC | Fixed OP | | Variable OP | |
| | | | | | 45 % | 7.4 % | 4 % TEC/yr | | 0.37 €/tFF | 85 % | 7.4 % | 4 % TEC/yr | | 0.18 €/tFF | |
| Base case in 2006 at 500 mg/Nm ³ NO _x | | | | | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SNCR | Cost-Effectiveness: Base to SNCR | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SCR | Cost-Effectiveness: Base to SCR | Incremental Cost-Effectiveness: SNCR to SCR |
| Unit | Design Feed | Utilisation | Actual Feed | Outlet NO _x | | | | | | | | | | | |
| | kt/yr | % | kt/yr | mg/Nm ³ | mg/Nm ³ | t/y | M€ | k€/yr | €/t NO _x | mg/Nm ³ | t/yr | M€ | k€/yr | €/t NO _x | €/t NO _x |
| 1 | 5480 | 97 % | 5319 | 500 | 275 | 299 | 22.9 | 4577 | 15297 | 75 | 565 | 114.4 | 13986 | 24745 | 35374 |
| 2 | 4081 | 91 % | 3693 | 500 | 275 | 208 | 19.2 | 3553 | 17100 | 75 | 392 | 95.9 | 11584 | 29520 | 43491 |
| 3 | 2857 | 88 % | 2506 | 500 | 275 | 141 | 15.5 | 2692 | 19100 | 75 | 266 | 77.4 | 9268 | 34813 | 52490 |
| 4 | 1388 | 82 % | 1131 | 500 | 275 | 64 | 10.0 | 1563 | 24565 | 75 | 120 | 50.2 | 5923 | 49278 | 77081 |
| 5 | 1648 | 99 % | 1625 | 500 | 275 | 91 | 11.1 | 1870 | 20459 | 75 | 173 | 55.6 | 6631 | 38411 | 58607 |
| 6 | 1927 | 97 % | 1877 | 500 | 275 | 106 | 12.2 | 2088 | 19777 | 75 | 199 | 61.1 | 7301 | 36604 | 55534 |
| Base case in 2006 at 400 mg/Nm ³ NO _x | | | | | Selective Non-Catalytic Reduction (SNCR) | | | | | Selective Catalytic Reduction (SCR) | | | | | |
| Unit | Design Feed | Utilisation | Actual Feed | Outlet NO _x | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SNCR | Cost-Effectiveness: Base to SNCR | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SCR | Cost-Effectiveness: Base to SCR | Incremental Cost-Effectiveness: SNCR to SCR |
| | kt/yr | % | kt/yr | mg/Nm ³ | mg/Nm ³ | t/y | M€ | k€/yr | €/t NO _x | mg/Nm ³ | t/yr | M€ | k€/yr | €/tNO _x | €/t NO _x |
| 1 | 5480 | 97 % | 5319 | 400 | 220 | 239 | 22.9 | 4577 | 19121 | 60 | 452 | 114.4 | 13986 | 30931 | 44218 |
| 2 | 4081 | 91 % | 3693 | 400 | 220 | 166 | 19.2 | 3553 | 21375 | 60 | 314 | 95.9 | 11584 | 36900 | 54364 |
| 3 | 2857 | 88 % | 2506 | 400 | 220 | 113 | 15.5 | 2692 | 23875 | 60 | 213 | 77.4 | 9268 | 43516 | 65612 |
| 4 | 1388 | 82 % | 1131 | 400 | 220 | 51 | 10.0 | 1563 | 30706 | 60 | 96 | 50.2 | 5923 | 61598 | 96351 |
| 5 | 1648 | 99 % | 1625 | 400 | 220 | 73 | 11.1 | 1870 | 25574 | 60 | 138 | 55.6 | 6631 | 48014 | 73259 |
| 6 | 1927 | 97 % | 1877 | 400 | 220 | 84 | 12.2 | 2088 | 24721 | 60 | 160 | 61.1 | 7301 | 45755 | 69418 |

Source: [139, CONCAWE 6/11 2011]

See also Table 4.18 for a cost comparison with other NO_x-reducing techniques.

Driving force for implementation

Reduction of NO_x emissions with limited space requirements.

Example plants

Several applications are known, e.g. in Japan.

Reference literature

[17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009], [105, EPA 2002], [151, Sema, Sofres 1991], [166, CONCAWE 1999], [228, TWG 2000].

4.5.4.3 Low-NO_x CO oxidation promoters**Description**

There is little, if any, contribution to NO_x from the thermal oxidation of N₂ in the catalytic cracking process itself, as the combustion in the regenerator takes place at reduced temperatures of less than 750 °C. In fact, NO_x released into the regenerator flue-gas is directly linked to the nitrogen contained in the feedstock. In the absence of feed nitrogen, no NO_x is formed and Pt-based CO promoters do not increase the overall emission from the FCC. Nearly half of the nitrogen in the catalytic cracker feed leaves the reactor as part of the coke laid down on the catalyst. Of the nitrogen in coke, about 80 % to 90 % is converted directly or indirectly to N₂ during regeneration, while the remaining nitrogen ultimately forms NO_x. Therefore, nitrogen oxides account for 5 – 10 % of the nitrogen introduced in the feedstock.

As shown in Figure 4.8, NO_x formation chemistry in the FCC regenerator is complex: the nitrogen in coke is pyrolysed and first appears in the regenerator as HCN or NH₃. These products are then oxidised in N₂, NO and NO₂, while a simultaneous reduction also takes place between NO and the available CO in order to regenerate gaseous N₂.

This technique only concerns the full combustion mode, where the aim is to burn the coke as fully and as efficiently as possible, and where conventional platinum-based CO combustion promoters are usually added which lower the CO concentration and enhance the oxidation of HCN, NH₃ and other reduced nitrogen intermediates to NO₂.

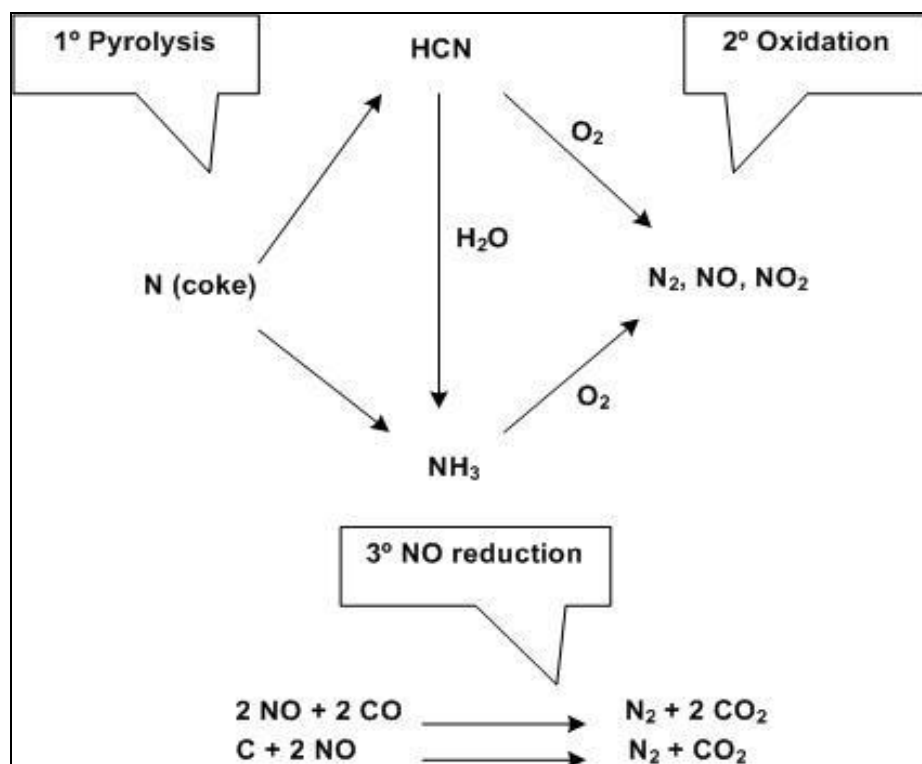


Figure 4.8: Simplified chemistry of the NO_x generation in FCC units

A first control option is to reduce the platinum load in the catalytic bed, either through minimising the addition rate or reducing the platinum content of the Pt-based CO promoter. However, as afterburning needs to be kept under control, this option can be limited.

Another alternative is to use low-NO_x non-platinum CO oxidation promoters. The non-platinum promoter selectively promotes the combustion of CO only and prevents the oxidation of the nitrogen which contains intermediates to NO_x. The addition rate of the non-platinum promoter is equal to two times that of the traditional platinum-containing promoter, depending on the regenerator operating conditions and excess oxygen level. The amount of non-platinum promoter is hence around 0.3 % w/w of the fresh FCC additive rate.

Achieved environmental benefits

Typical downstream effluent NO_x concentrations of 40 – 140 mg/Nm³ (daily average) at 3 % O₂ are reported for a feedstock nitrogen content of approximately 0.20 %. The amount of NO_x avoided depends on the amount of additive in the unit, but the removal efficiency is typically between 30 % and 50 %.

When combining both low-NO_x non-platinum CO oxidation promoters and NO_x removal additives (see Section 4.5.8.4), or when using specific products which combine the two functions, structurally NO_x reduction of more than 80 % is achievable, depending on the added quantity.

Cross-media effects

None in particular.

Operational data

See Section 4.5.4.4.

Applicability

A low-NO_x non-Pt CO promoter is an option for NO_x reduction in full combustion FCC units already using a Pt-based CO promoter. It is not applicable at all for partial-burn FCC units. The

application of the additives is not specifically dependent on the FCC unit design. However, proper distribution of air in the regenerator is required to obtain the maximum benefit. No significant deterioration in unit performance is reported, nor any increase or decrease in the catalyst replacement rate. In addition, care must be taken to optimise the dosage of both Pt-based and non-Pt promoters to assure that the unit is not generating more NO_x.

Economics

Table 4.18 gives rough cost estimates reported for various control approaches for a typical 28 000 bpd (1.6 Mt/yr) FCC unit.

Table 4.18: Cost comparison of catalytic additives with other NO_x control techniques for a FCC unit

| Technique | Expected efficiency (%) | Installation cost 2008 (USD million) | Operational cost 2008 (USD million/yr) | Specific removal cost (USD/tonne NO _x) |
|---|-------------------------|--------------------------------------|--|--|
| SCR | 85 | 2.1 – 6.3 | 0.21 – 0.84 | 3 600 |
| SNCR | 60 – 80 | 0.6 – 2.6 | 0.09 – 0.70 | 3 000 |
| Low-NO _x promoter ⁽¹⁾ | 40 – 70 | – | 0.32–1.76 (1) | 1 200 – 3 600 |
| Specific NO _x reduction additive | 30 – 80 | – | 0.11 – 0.22 | 2 400 – 3 600 |

⁽¹⁾ Incremental cost compared with a Pt-based promoter.

In addition, cost data for using SCR and SNCR are detailed in Table 4.17.

The cost for removing NO_x with such a low-NO_x CO promoter will depend on the regenerator operating conditions and the actual mechanical design of the promoter. It is estimated that on average the cost will vary between EUR 1 and EUR 5 per kg NO_x removed.

Driving force for implementation

A noticeable reduction of NO_x is achieved while no capital expenditure is required.

Example plants

Many refineries (around 40 units alone in the USA) have applied non-Pt CO combustion promoters to the catalyst. The method is well established commercially.

Reference literature

[23, Yaluris et al.2006], [26, Kramer et al.2009], [27, Vierheilig et al.2003], [36, CONCAWE n°4/09 2009], [89, Galp 2011].

4.5.4.4 Specific additives for NO_x reduction

Description

As a complementary or substitutional approach to non-Pt low-NO_x CO promoters, this technique consists of using specific catalytic additives for enhancing the further reduction of NO by CO. These additives capitalise on the inherent concentration gradients of gases maintained in the regenerator, and catalyse those chemical reactions which belong to the third group as displayed in Figure 4.8. So far, they have proven to be efficient only for the full combustion mode. The additives can be used alone, in combination with conventional Pt-based promoters, or together with low-NO_x CO promoters, depending on the operational conditions of the unit.

Achieved environmental benefits

Results are highly variable and depend on the unit design (regenerator), feed quality (normal operation fluctuations), catalyst selection, and the achievable oxygen excess. Reductions of

NO_x emissions of up to 80 % are reported when used in favourable conditions, either alone or in combination with a Pt-based conventional CO promoter. However, such reduction levels remain exceptional and typical reductions more often observed range from around 40 % to >60 %. [141, TWG FI 2012]. Figure 4.9, from around 30 applications (data from a DeNO_x additives supplier), illustrates the typical achieved reduction range with the use of additives.

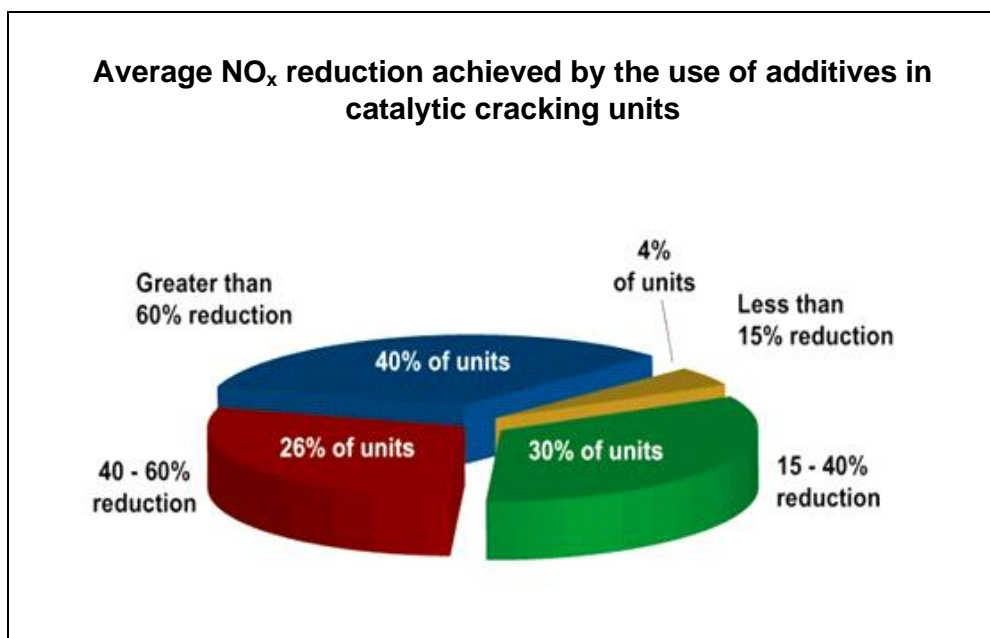


Figure 4.9: Achieved NO_x reduction from the use of additives in catalytic cracking units

As shown in Table 4.19, results also depend on the initial NO_x concentration to be abated in the FCC regenerator.

Table 4.19: Various NO_x additive performances reported in full combustion FCC units operated in the US

| Type of additive ⁽¹⁾ | NG-A | NG-A | NG-B | NG-B | NG-B | NG-B | NG-B |
|--|----------|------------|-----------|-----------|------|-----------|--------|
| FCC design | Model IV | Ortho-flow | UOP stack | UOP stack | HOC | Model III | UOP HE |
| Regenerator bed temperature (°C) | 710 | 706 | 721 | 718 | 721 | 740 | 740 |
| Initial NO _x concentration (ppm) ⁽²⁾ | 125 | 160 | 65 | 69 | 67 | 137 | 90 |
| Final NO _x concentration (ppm) ⁽²⁾ | 30 | 63 | 47 | 45 | 44 | 57 | 45 |
| NO _x reduction (%) | 76 | 61 | 28 | 35 | 34 | 58 | 50 |
| Additive concentration ⁽²⁾ (%) | 5 | 5 | 1 | 1 | 1 | 0.5 | 1 |

⁽¹⁾ These types correspond to two different technologies based on different chemical actions for affecting NO_x reduction. They are developed by the same supplier and can be selected after a minimum 8-day real-run trial.
⁽²⁾ Expressed in % of the total catalyst addition.
⁽³⁾ NB: 20 ppmv at 0 % O₂ of NO_x is around 32 mg/Nm³ at 3 % O₂.

Figure 4.10 gives more details on the NO_x reduction that was obtained for a high capacity (110 000 barrels/day – 6 Mt/yr) full combustion FCC unit operated in the US, with a NO_x-reducing additive incorporated intermittently during two years of trials, at concentrations

never exceeding 1 % of the catalyst inventory. In this specific case, it was observed that when such an additive was used in conjunction with a conventional Pt-based CO promoter the NO_x reduction was even greater than when used alone [27, Vierheilig et al.2003].

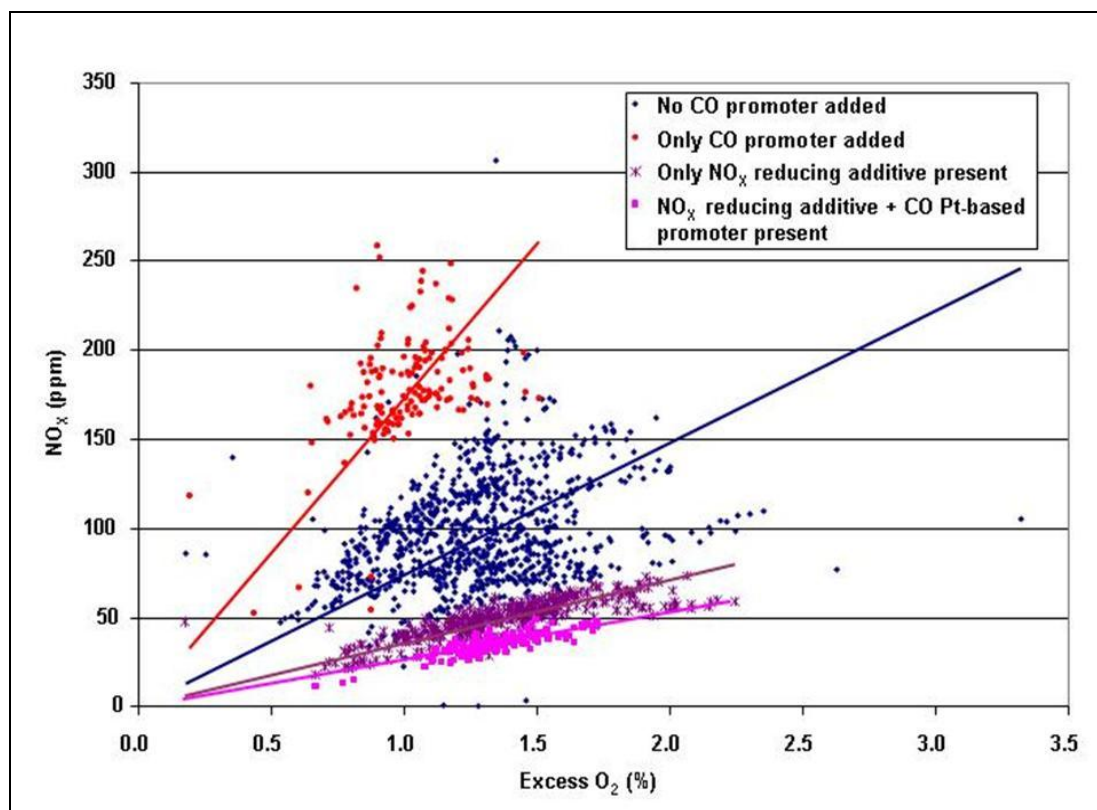


Figure 4.10: Full combustion FCC NO_x emissions as a function of excess O_2 in various catalyst additive configurations

When used in combination with a low- NO_x CO promoter as shown in Figure 4.11, a further reduction of up to 40 % can be obtained on the residual NO_x level, depending on the mutual additive rates chosen for the given unit. However, the adjustment of such a catalyst mixture CO promoter/additive for a given installation must be carefully evaluated and tested on a case-by-case basis.

Cross-media effects

Copper-based NO_x -reducing additives can also promote the production of hydrogen and create difficulties for FCC units operated at their gas compression capacity limits.

Operational data

Figure 4.11 gives an overview of the results obtained on a large 4.5 million t/yr FCC unit, operated in full combustion mode, after pretreatment with a low- NO_x non-Pt CO promoter. As shown, the NO_x -reducing additive is incorporated both by using one-shot monthly doses together with continuous addition at an increasing rate into the fresh catalyst renewal stream. After a three-month trial, NO_x emissions tended to stabilise at around 40 % below the original average.

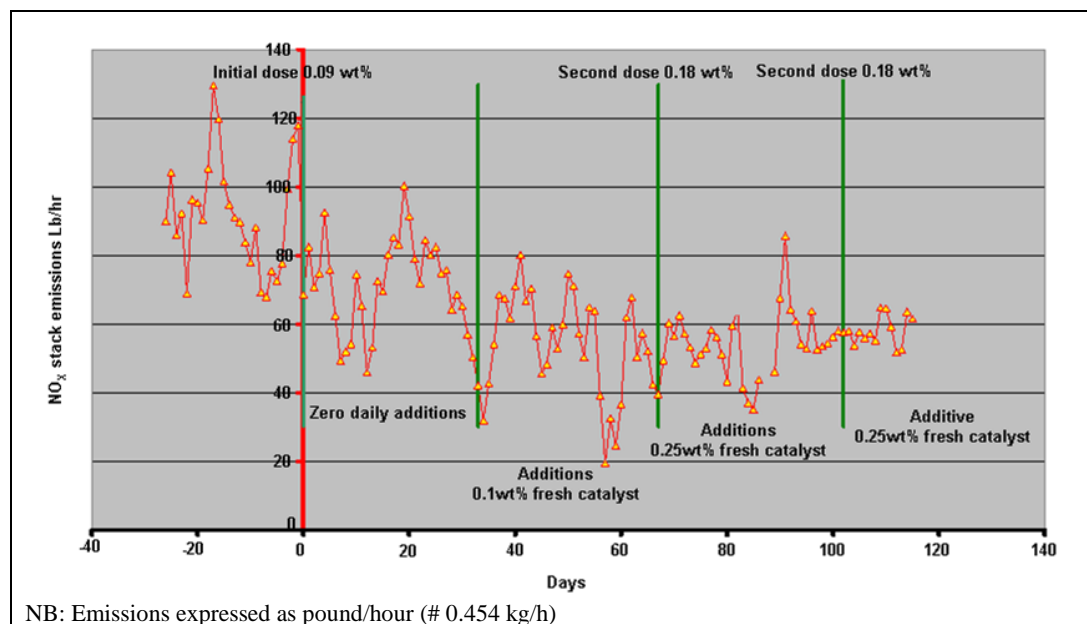


Figure 4.11: Performance obtained with a NO_x-reducing additive in a full combustion FCC unit

The use of a non-Pt low-NO_x CO promotor was experimented with at a refinery in Portugal, at the beginning of 2010. At the end of the test period, it is reported that the replacement of the previous combustion promotor led to an 80 % reduction of NO_x emissions in the flue-gas with 80 ppm (about 130 mg/Nm³) NO_x concentration. In addition, the emissions are reported to be stable, and no longer depend on the nitrogen level in FCC feed [89, Galp 2011].

Applicability

This technique is proven to be efficient only in the full combustion mode.

The performances of such additives are naturally sensitive to the available concentration of CO as one of the reactants. Thus, low excess oxygen conditions favour their efficiency.

Even if good results are obtained with a combination of Pt-based conventional promotors, the logical approach is to first reduce the generation of NO_x at source as much as possible by using low-NO_x CO promotors, and then use the additives as complementary.

By 2008, there were four commercially available NO_x reduction additives, of which three were copper-based.

Applicability may be limited, for FCC units operated at their gas compression capacity limits, by the increased production of hydrogen caused by the copper, if present, in the additive. More generally, the technique is sensitive to numerous parameters and therefore, retrofitting requires preliminary tests to determine NO_x reduction.

Economics

See Table 4.18 in Section 4.5.4.3. The option of using such additives in combination with a low-NO_x non-Pt CO promotor compared with using them alone is very often the most economically sound solution, as NO_x-reducing additives are added at rates of 0.5 – 2 % of fresh catalyst renewal, while CO promotors are added at much lower rates of 5 – 10 kg/day.

Driving force for implementation

To achieve a further reduction of NO_x emissions with little or no additional capital costs.

Example plants

According to equipment suppliers, this technique is said to be currently used by around 20 refineries in the US. In Europe, this technique is also used, e.g. at one refinery in Portugal.

Reference literature

[24, Bruhin et al.2003], [26, Kramer et al.2009], [27, Vierheilig et al.2003], [30, Sawyer et al.2009], [36, CONCAWE n°4/09 2009], [141, TWG FI 2012].

4.5.4.5 Low-temperature oxidation (SNERT process/LoTO_x technology)**Description**

See Section 4.23.3.1.

Achieved environmental benefits

The reduction of NO_x emissions from a FCC unit by 85 – 95 %, with an outlet concentration reduced to 10 ppm (14 mg/Nm³ NO_x under EU reference conditions (0 °C, 3 % O₂), 95 % NO - 5 % NO₂).

Cross-media effects

The SNERT/LoTO_x process operates optimally above 150 °C and does not require heat input to maintain operational efficiency, enabling maximum heat recovery from the flue-gas.

Nevertheless, SNERT/LoTO_x is associated with a new or existing scrubbing unit, which generates waste water to be treated properly. An increase in nitrate load to the existing WWTP may have to be considered, together with the associated cost to control nitrates.

Nitric acid is produced and needs to be neutralised with an alkali used in the scrubbing section. In order to oxidise the NO_x to soluble higher oxides, ozone is required and should be generated on site using an ozone generator, which consumes oxygen and electrical energy.

Operational data

NO_x removal performance is directly linked to the ozone injection rate and its real-time regulation in relation to the NO_x outlet concentration target. The outlet NO_x can be adjusted by varying the set point on the system controller. In Figure 4.12, the set point was set in order to respect the permit conditions of 20 ppm (27 mg/Nm³ NO_x).

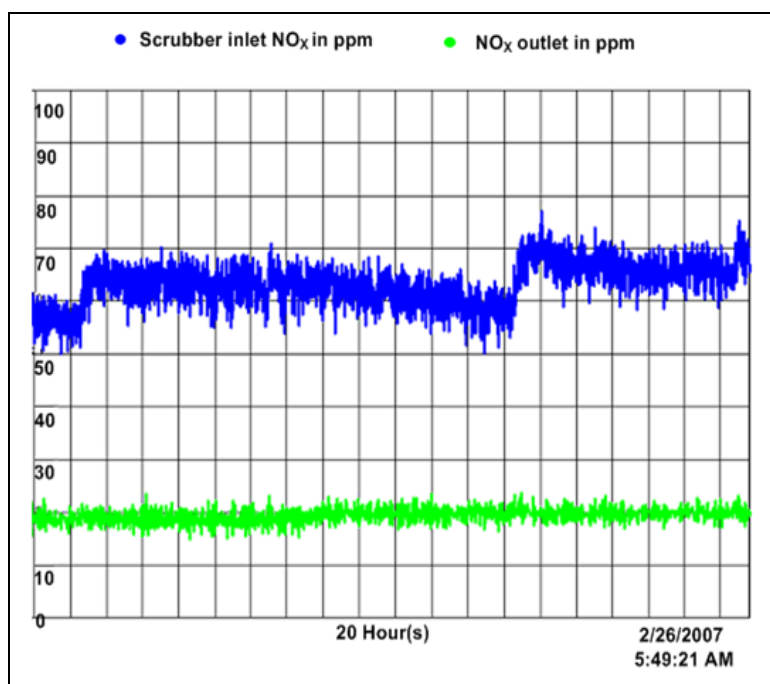


Figure 4.12: Initial results of commercial operation at a US (Texas) refinery FCC unit - 2007

Applicability

The first demonstration tests on the FCC unit were conducted in 2002. Between 2007 and 2009, low-temperature oxidation units have been implemented in seven FCC units, of which six are operated in the US and one in Brazil. Four of them have been retrofitted on existing scrubbers, one of them was not originally installed by the LoTO_x patenting equipment supplier. In the case of retrofitting, a separate tower may have to be built in order to provide the required additional ozone injection and reaction stage. Ozone slip out of the stack will be associated with this technology. Appropriate design for additional processes related to ozone generation and personnel safety have to be taken into account.

The applicability may be limited by the need for additional waste water treatment. It should also be taken into consideration that an appropriate supply of liquid oxygen for ozone generation is needed. The applicability of the technique may also require significant space availability.

Economics

In 2005, potential investment and operational costs for implementing this technology on two FCC units in Colorado refineries (US) were estimated in a range of USD 1 900 – 2 100 per year and tonne of NO_x avoided, assuming a related NO_x emission decrease of 85 – 90 %. Additional costs associated to nitrates control in the waste water may also need to be considered.

Driving force for implementation

The main advantages of the LoTO_x process are: NO_x selectivity, adjustability of NO_x removal performances, absence of interference with the FCC unit chemical process and operating conditions (including O₂ concentration in the flue-gas), compatibility with flue-gas energy recovery, and relative ability to handle unit upsets without impacting overall reliability and mechanical availability.

Example plants

US Refineries: BP (Texas City), Flint Hills (Corpus Christi), Lion Oil (El Dorado), Marathon (Texas City), Valero (Houston and Texas City), Western Gaint (Gallup).

Reference literature

[17, Jeavons and Francis 2008], [18, Confuorto 2007].

4.5.4.6 Process optimisation

Description

The FCC operating conditions and practices can be adjusted in order to reduce the NO_x formation. This ensemble of process optimisation techniques includes but is not limited to:

- reducing excess oxygen in the flue-gas,
- lowering the regenerator bed temperature,
- operating air staging in the CO boiler where present (in partial combustion mode).

Achieved environmental benefits

Dependent on design and operating conditions of the CO boiler (see below).

Environmental performance and operational data

A number of trials have been carried out at a German refinery site in order to determine the maximum NO_x reduction achievable by operating air staging in a CO boiler (FCC in partial combustion mode). By varying the airflow on the three air feed points, 'burners 1 – 3', '1 stage' and '2 stage' (post-combustion), the NO_x content in the FCC flue-gas can be reduced by up to 100 mg/Nm³. This has been achieved by shifting the combustion air from the burners to the second stage.

Starting from an initial value of approximately 375 mg/Nm³ (without air to the second stage), the NO_x in the flue-gas could be reduced at the end of the test to about 270 – 290 mg/Nm³ (at around 14 000 Nm³/h air to the second stage), without negatively affecting the CO combustion or the combustion chamber temperatures of the boiler.

The results suggest that, with this particular configuration and operating conditions (7.5 % v/v CO in the regenerator flue-gas, feed nitrogen content 300 – 400 mg/kg), an average emission limit of 350 mg NO_x/Nm³ can be achieved without the use of secondary measures.

Cross-media effects

To achieve a maximum CO burn, an O₂ excess of at least 2.0 – 2.2 % v/v is required. Below this value, the CO conversion is incomplete and may lead to high CO releases.

A positive side effect of using air staging can be that furnace temperatures tend to rise through the reduction of air to the burners and, therefore, the additional firing needed to maintain the firebox temperature can be reduced slightly.

Technical considerations relevant to applicability

It is reported from some trials that the achieved results are strongly dependent on the design of the CO boiler and the current plant configuration. The maximum possible reduction would need to be determined on a case-by-case basis.

Economics

Very limited costs as no investment is required and only process fine-tuning is used.

Driving force for implementation

CO and NO_x emissions control.

Example plants

Some trials have been performed at a German refinery site (see Environmental performance and operational data above). These trials consist of air staging carried out in order to determine the maximum possible NO_x reduction in the FCC flue-gas through optimal distribution of the CO boiler combustion air supplied at a constant CO content in the regenerator.

Reference literature

[130, Reza Sadeghbeigi 2012], [142, TWG DE 2012].

4.5.5 Particulate abatement techniques

The selection of the catalyst has an impact on particulate emissions, but will not be considered in this section. That technique has been included in Section 4.5.3, together with other possible aspects of catalyst replacement.

4.5.5.1 Third-stage cyclone separators

Description

Third-stage separators (TSS) are a cyclonic collection device or system installed following the two stages of cyclones within the FCC unit. The most common configuration of a TSS consists of a single vessel containing many conventional cyclones, or may be new, improved swirl-tube technology (e.g. Shell Global Solutions, or CycloFines™). TSS is a common choice as a clean-up device for particulates and as an aid to energy efficiency. The first attempts at power recovery from FCC unit regenerator flue-gas were unsuccessful because the expander blade lifetimes were limited to a few weeks. It was found that particle sizes of 10 micron and larger were particularly harmful to the blades. TSS were introduced to protect power recovery expander turbines from particulate damage. Recent advances in this technology, as shown in Figure 4.13, favour, in particular, the use of a large number of axial flow swirl tubes of relatively small diameter, in order to induce a fast rotating motion and handle the large volume of flue-gas in more compact vessels. They are high-velocity devices and the recovered catalyst is returned to a dust hopper. In some cases, a new stage of filtration is used and they are then named fourth stage.

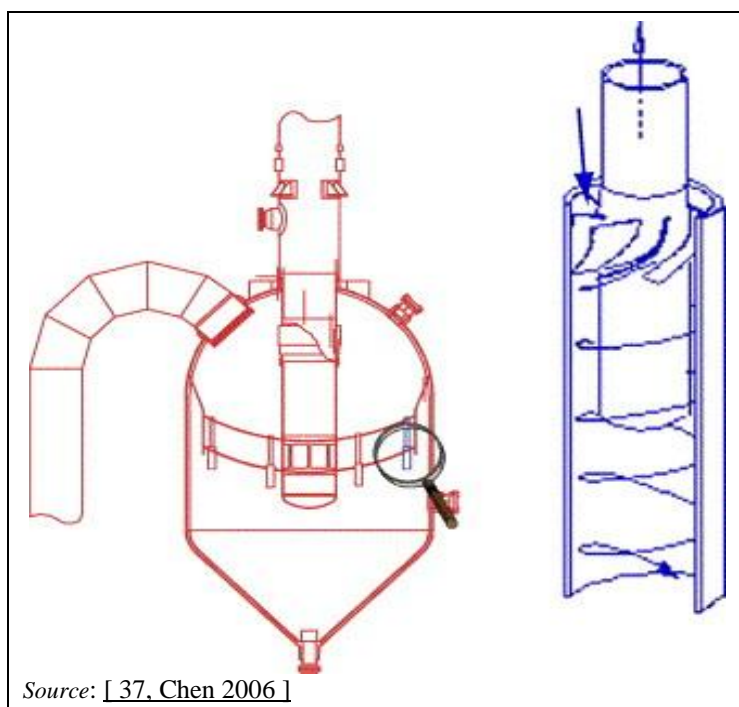


Figure 4.13: Scheme of a TSS using multiple-axial swirl-tube technology

Achieved environmental benefits

The average performance outlet concentration for an advanced TSS is $<50 - 100 \text{ mg/Nm}^3$, depending on the inlet particulate concentration and size distribution. Lower concentrations are not achievable because inlet velocities to the cyclones are in the region that causes additional attrition, which produces additional fines that pass through the cyclone.

Depending on the above factors and on the type of technology used, cyclones are generally efficient at removing particles larger than 10 – 40 microns. Recent swirl-tube devices allow a 50 % cut point of about 2.5 microns. Efficiencies can range from 30 % to >90 %. For inlet concentrations below 400 mg/Nm³, the efficiency can only exceed 75 % for a particulate size distribution with a median (by mass) of >5 microns.

By reducing the particulate content in the air, the metal emissions are also reduced.

Cross-media effects

Catalyst fines recovered containing some hazardous metals are classified as hazardous industrial waste and have to be properly handled and eliminated in order to avoid any pollution transfer from air to water and soil.

Operational data

Catalyst fines removal is typically 300 – 400 tonnes/yr per unit. A TSS generates a pressure drop in the flue-gas. Good performance and reliability in many FCCs have been demonstrated. Table 4.31 shows emissions data from continuous monitoring, including dust, of a sample of European FCC units (see Section 4.5.7). The FCC units equipped with third-stage separators (TSS) only (no additional device) report dust emissions in the range of 80 – 150 mg/Nm³, as a monthly average.

Applicability

TSS are applicable to any FCC, but their performance will vary considerably, mainly depending on the particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones. These abatement devices are very often used in combination with other abatement techniques such as ESPs.

Economics

Table 4.20 shows economic data for third-stage cyclones used in FCC

Table 4.20: Economic data for third-stage cyclones applied to FCCs

| Size of the FCC (Mt/yr) | Efficiency (%) | Downstream particulate concentration (mg/Nm ³) | Investment (EUR million) | Operating cost (EUR million/yr) |
|-------------------------|----------------|--|--------------------------|---------------------------------|
| 1.5 | 30 – 40 | 40 – 250 | 1 – 2.5 | 0.7 |
| 1.5 | 30 – 90 | 60 – 150 ⁽¹⁾ | 0.5 – 1.5 | 0.1 |
| 1.2 | 75 | 50 – 100 ⁽²⁾ | 1.5 – 2.5 | |

⁽¹⁾ Initial concentration: 450 mg/Nm³ (300 – 600 mg/Nm³ range).
⁽²⁾ Initial concentration: 200 – 1000 mg/Nm³.
 NB: Operating costs include only direct cash operating expenses, i.e. they do not include the depreciation of investment, or financial charges. Investment costs refer to new plant installation. Economics do not include the cost of disposal of the waste generated.

The cost of disposal for the fine catalyst is around EUR 120 – 300 per tonne, including transportation.

Driving force for implementation

TSS control particulate emissions and protect downstream equipment such as heat or power recovery units (e.g. expander blades).

Example plants

Many FCC units are operating with these systems.

Reference literature

[36, CONCAWE n°4/09 2009], [151, Sema, Sofres 1991], [156, MCG 1991], [166, CONCAWE 1999], [221, Italy 2000].

4.5.5.2 Electrostatic precipitators (ESPs)

Description

A short description of the basic principles of an electrostatic precipitator can be found in Section 4.23.4.

Particle resistivity is a key factor for the efficiency of the ESP. The following parameters are generally reported to lower the resistivity of the particles in order to improve the collection efficiency of the electrostatic precipitator used for a catalytic cracking unit flue-gas:

- higher inlet temperature;
- higher concentration of metals, rare earth or carbon in the catalyst;
- moisture content;
- ammonia injection.

Achieved environmental benefits

Typical concentrations achieved with electrostatic precipitators are usually $<20 - 50 \text{ mg/Nm}^3$ as a daily average based on continuous monitoring under normal operating conditions (e.g. excluding soot blowing in the CO or auxiliary boilers' end-of-run conditions).

When available for shorter averaging periods, values of total particulate matter in the flue-gas of the FCC regenerator of $<50 \text{ mg/Nm}^3$ as an hourly average are reported or included in permits (e.g. in Germany, see under Operational data). As a consequence of the particulate reduction, metals (Ni, Sb, V and their components) can be reduced to less than 1 mg/Nm^3 (given as Ni, Sb and V total) and, within that, Ni by itself and its components can be reduced to less than 0.3 mg/Nm^3 (given as Ni), all concentrations being expressed as half-hourly mean values attainable in continuous operation and with soot blowing in the CO boiler.

Cross-media effects

The refinery may need extra facilities to manage the fine particulates (catalyst) recovered that require disposal. The high voltage in an ESP introduces a new safety risk in refineries and leads to increased operating costs for electricity and maintenance. For some installations, ammonia may be injected to improve the ESP performance (as a resistivity attenuation agent). For these installations, ammonia emissions result from ammonia slip through the ESP. Safety concerns are also expressed about the use of ESPs during the FCC start-up process. Special care must be taken to ensure that uncombusted hydrocarbons are never allowed to enter the ESP itself, as the sparking environment may result in an explosion. [[31, BARPI 2009](#)], [[36, CONCAWE n°4/09 2009](#)].

Operational data

The particulate abatement efficiency with an ESP in FCC is usually much greater than 90 %. The actual concentration range achieved at the ESP outlet will depend on the residence time (i.e. the ESP size), the properties of the particulate (i.e. catalysts), the mode of FCC operation, the flue-gas temperature, and whether other particulate removal devices are installed upstream of the ESP. In usual conditions, a residence time greater than 30 seconds would be necessary to achieve very low concentrations ($<10 \text{ mg/Nm}^3$). Particle size can also affect the ESP efficiency, since very fine particulate ($<2 \text{ }\mu\text{m}$) is more readily re-entrained during the cleaning cycle (rapping) of the ESP electrodes.

Electrostatic precipitators add a small pressure drop to the system; higher pressure drops may result from the inlet and outlet ducting to the ESP. In some cases, a forced draft or induced draft fan may need to be added. The extra energy consumption (electricity) is typically low, but can be significant for ESPs with long residence times. ESPs also require regular maintenance to ensure high capture efficiency. Information from some EU refineries shows that the use of deep desulphurisation of the feedstock can have a great impact on ESP performance (because the content of sulphur and metals is lower), reducing the ESP efficiency. In these cases, achievable particulate emissions have been reported to be $30 - 35 \text{ mg/Nm}^3$.

Figure 4.14 and Figure 4.15 show a one-year profile of the daily average concentration achieved by two ESPs operated in two German FCC units.

- Results for the first FCC displayed in Figure 4.14 are achieved under normal operating conditions, using a filtering configuration consisting of a conventional set of internal cyclones, an additional external cyclone and a 4-field ESP. The yearly average concentration is 10.94 mg/Nm^3 , with a standard deviation of 9.62, and the maximum recorded daily average is nearly 37 mg/Nm^3 . The typical daily average concentration is rather variable, mostly within the range of $5 - 25 \text{ mg/Nm}^3$.
- In comparison, the second FCC (Figure 4.15) has a simpler configuration, with only a combination of an internal cyclone and a 2-field ESP. Moreover, this one-year period includes a shutdown/start-up step (identified on the graph) during which emissions were significantly higher than for stable conditions. The yearly average is 10.16 mg/Nm^3 (calculated from daily values different from zero) with a standard deviation of 5.2. Even though the maximum recorded daily average value of 38 mg/Nm^3 is comparable to the first ESP (Figure 4.14), the typical daily average concentration during stable operating conditions is much more constant, staying mostly within the range of $5 - 15 \text{ mg/Nm}^3$.

Particulate emissions can increase after a FCC turnaround due to higher solids loading to the ESP. This can be attributed to higher attrition of new catalyst that may be loaded after a turnaround.

The following data for a German FCC plant are reported, after the ESP (no cyclone) in the waste gas of the CO boiler (normal operation):

- emission limit values in the permit:
 - total particulate matter, daily average value: 30 mg/m^3 ;
 - 30-minute average value: 60 mg/m^3 ;
- monitoring data: total PM: $13 - 23 \text{ mg/m}^3$ (30 minutes, $\text{O}_2 = 3.1 \%$, 100 % capacity utilisation, feed 80 % atmospheric residues, 20 % heavy wax distillates).

Another similar FCC with a cyclone and ESP abatement techniques is reported to achieve PM levels of $9 - 21 \text{ mg/m}^3$ (100 % capacity with feed: 50 % vacuum gas oil, 40 % atmospheric residue, 10 % others). *Source: TWG 2010-DE.*

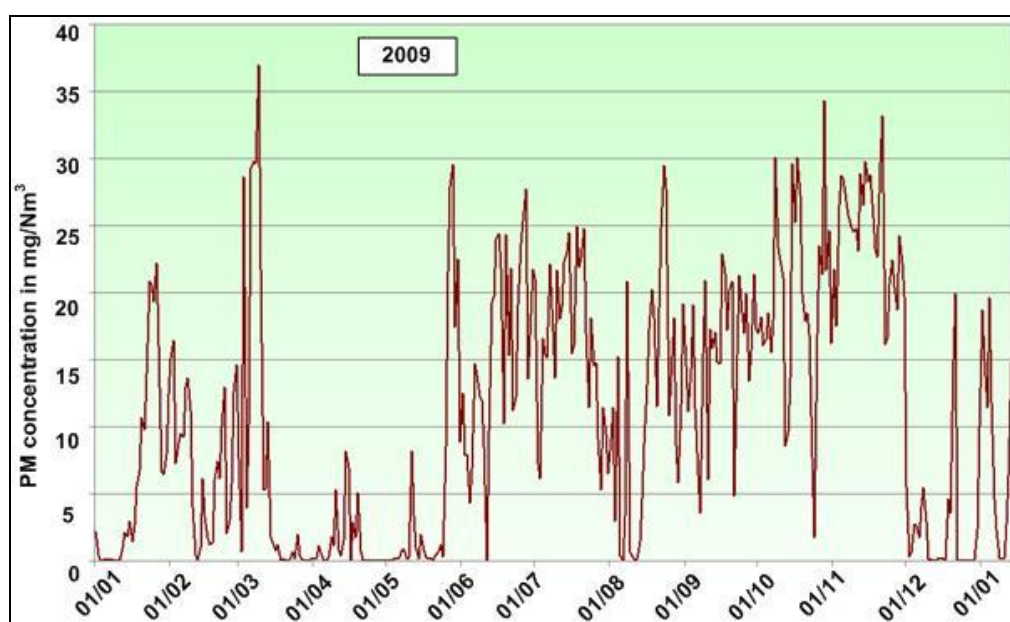


Figure 4.14: Daily average PM concentrations achieved by an ESP on a German FCC unit

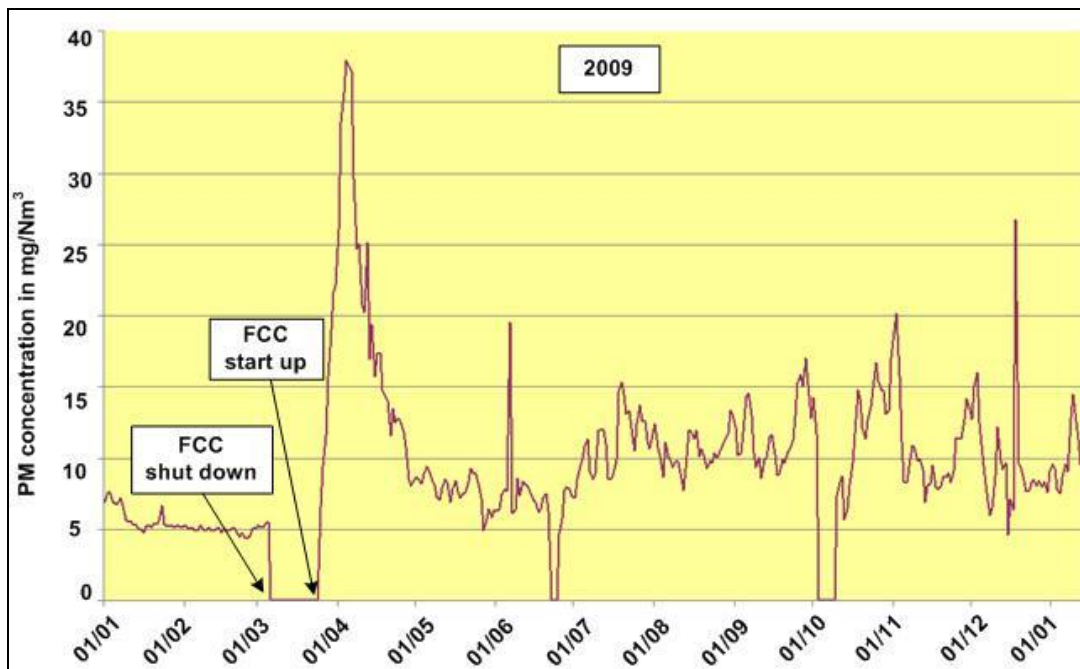


Figure 4.15: Daily average PM concentrations achieved by an ESP on a German FCC unit

Additional data linked to the TWG data collection questionnaire number 18 show dust emissions from a recent (built in 2008) ESP on a full combustion mode FCC (see Figure 4.16).

After a period of process development, isokinetic measurements (60-minute sampling – year 2011) show the following values:

- 20 – 25 mg/Nm³ in normal operating conditions;
- 30 – 40 mg/Nm³ during soot blowing.

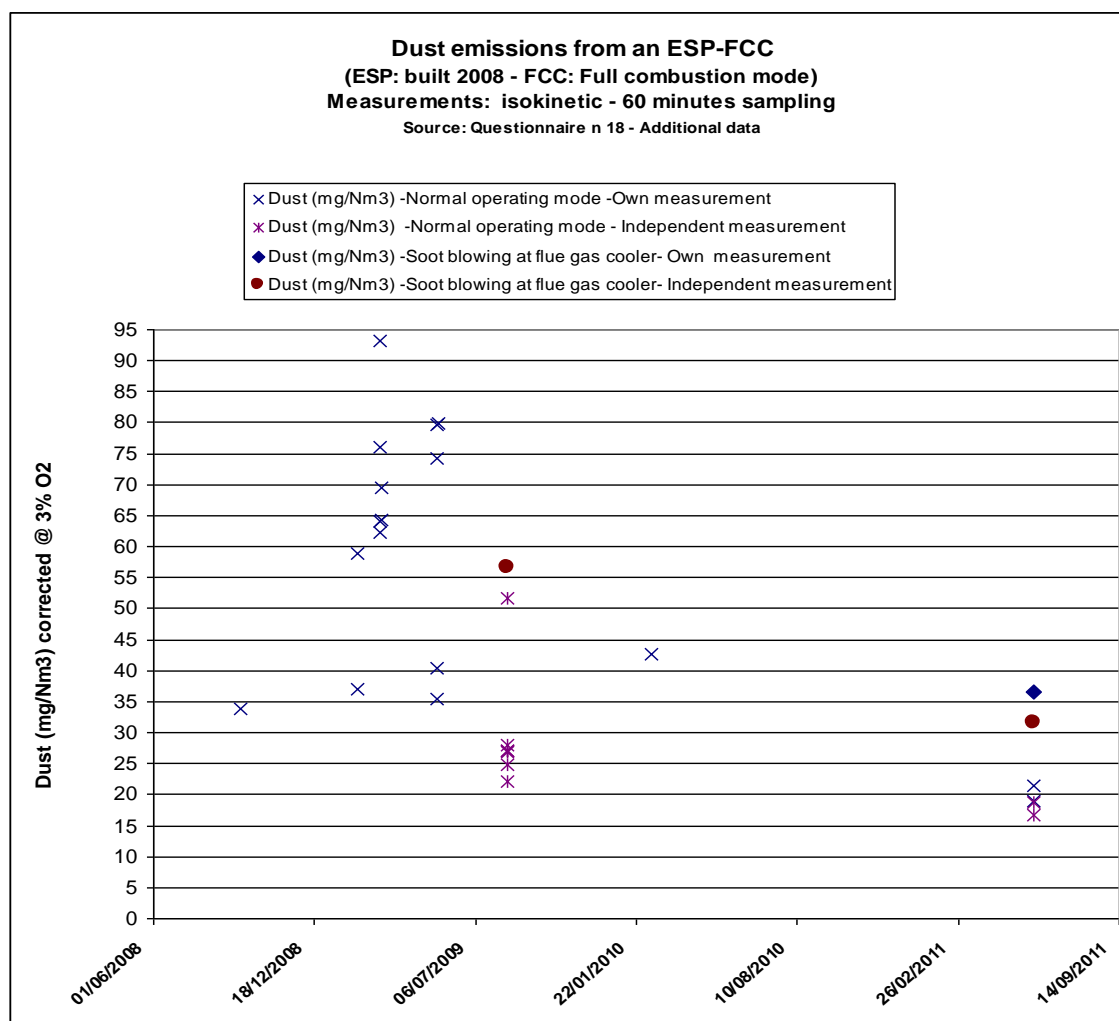


Figure 4.16: Reported dust emissions (isokinetic measurements) from a FCC unit equipped with an ESP (TWG Questionnaire number 18)

Figure 4.17 shows the distribution of daily values of dust emissions (2011) from a German FCC processing desulphurised vacuum diesel and equipped with an ESP, installed in 2007 in addition to an existing third-stage cyclone.

A compilation of the emissions data from continuous monitoring, including dust, of a sample of European FCC units is shown in Table 4.31 (see Section 4.5.7). The FCC units equipped with ESPs report dust emissions in the range of 10 – 50 mg/Nm³ as a monthly average. Among these, the ones equipped with a combination of tertiary cyclones and a 4-field ESP perform better and in the range of 10 – 25 mg/Nm³.

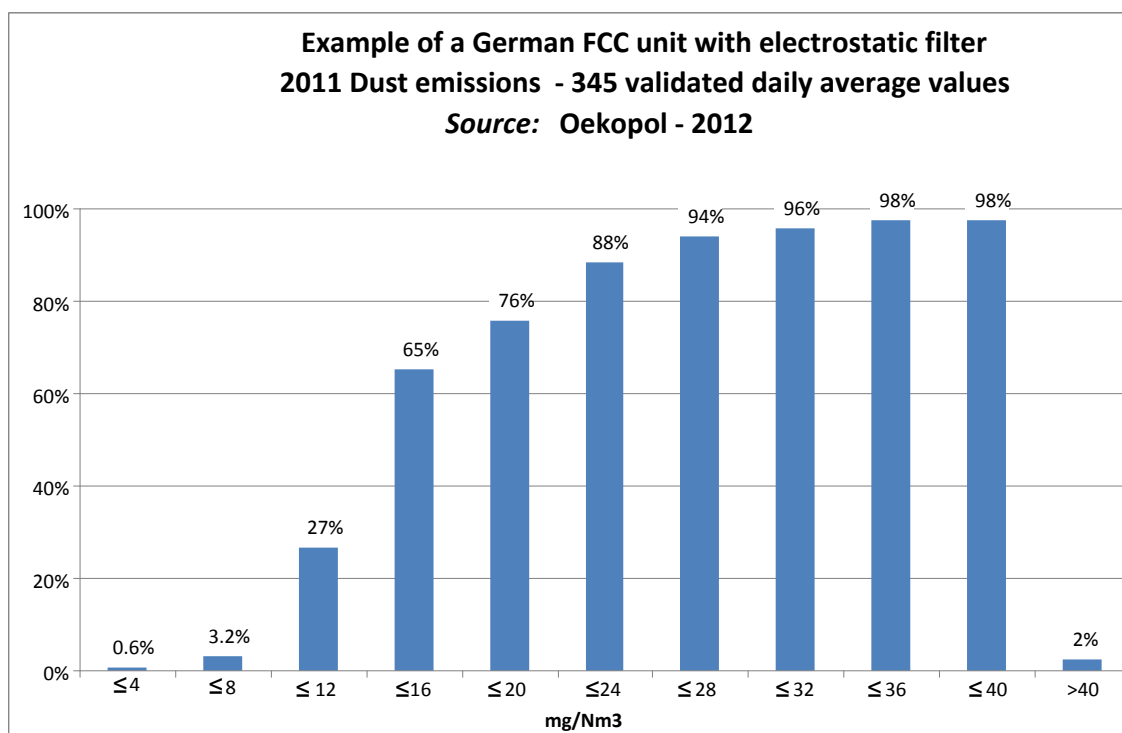


Figure 4.17: Reported distribution of daily dust emissions values from the continuous monitoring of a German FCC equipped with an ESP

Applicability

ESPs require significant plot space, especially when they are sized to achieve very low particulate emission levels. A large plot space is required because FCC outflows are typically large (a 1.5 Mt/yr FCC generates 2.8 million Nm³/day of flue-gas). An ESP requires low internal velocity and therefore large volumes at typical design residence times to achieve the required performance levels. In order to not exceed gas flow speed specifications, the ESP performance may be adversely affected if the particulate has a high electrical resistivity. In addition, deep hydrotreatment of the FCC feedstock will lower the catalyst metal content, reduce conditioning agents (SO₃) in the flue-gas and therefore reduce the collection efficiency. Also worth mentioning is that the performance of ESPs is likely to degrade from the start to the end of the FCC run. This may be due to ESP maintenance issues, which require a shutdown, and/or the potential for increased attrition/loss of catalyst particles at the end of run. Finally, ESPs may not cover start-up and shutdown periods and will have to be electrically isolated due to the safety reasons already described.

Economics

Available data have been gathered in Table 4.21 and additional information on costs for comparison of various filtration devices (tertiary cyclones, 3-field ESP and 4-field ESP) is presented in Table 4.22.

Table 4.21: Economic data of ESPs applied to FCCs

| Size of the FCC (Mt/yr) | Efficiency (%) | Downstream PM concentration (mg/Nm ³) | Investment (EUR million) | Operating cost (EUR million/yr) |
|-------------------------|--------------------|---|--------------------------|---------------------------------|
| 2.4 | >50 ⁽¹⁾ | <50 ⁽¹⁾ | 15 – 30 | 0.15 ⁽²⁾ |
| 1.5 | – | <30 | 2.05 ⁽³⁾ | - |

⁽¹⁾ Unabated concentration >100 mg/Nm³ → Abatement target <50 mg/Nm³.
⁽²⁾ 2009: respectively USD 20 – 40 million (installed capital cost) and USD 0.2 million [30, Sawyer et al.2009].
⁽³⁾ 2008: HUF 1.3 billion for the whole ESP project.

Table 4.22: Cost data of various FCC filtration devices

| Assuming Base Case Dust at 100mg/Nm ³ | | | | | | | | | | | | | | | | | | | | | |
|--|-------------|-------------|-------------------------------|--------------------------|---|--------------------------------|-----------------------------------|--|-----------------------------------|---|--------------------------|--------------------------------|--------------------------------|-----------------------------------|--|--------------------|--------------------------|--------------------------------|--------------------------------|-----------------------------------|--|
| Base Case in 2006 | | | | | Electrostatic Precipitator 3-Fields (ESP-3) | | | | | Electrostatic Precipitator 4-Fields (ESP-4) | | | | | | | | | | | |
| | | | | | | | | | Outlet dust | Efficiency | ACC | Fixed OP | Variable OP | Outlet concentration | | | | | | | |
| | | | % | % | %TEC/yr | %TEC/yr | mgDust/ Nm ³ | | mg/Nm ³ | % | % | %TEC/yr | %TEC/yr | mgDust/Nm ³ | | | | | | | |
| | | | 90 % | 7.4 % | 4 % | 1 % | 30 | | 50 | 90 % | 7.4 % | 4 % | 1 % | 30 | | | | | | | |
| | Design Feed | Utilisation | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ESP-4 | Cost-Effectiveness: Base to ESP-4 | Incremental Cost-Effectiveness: ESP-3 to ESP-4 | Cost-Effectiveness: Base to ESP-3 | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ESP-4 | Cost-Effectiveness: Base to ESP-4 | Incremental Cost-Effectiveness: ESP-3 to ESP-4 | | | | | | |
| | kt/yr | % | mg/N _{m³} | t/yr | ME | k€/yr | €/tDust | €/tDust | mg/Nm ³ | t/yr | ME | k€/yr | €/tDust | €/tDust | €/tDust | | | | | | |
| Unit 1 | 5 480 | 97 % | 30 | 93 | 32.5 | 4 029 | 43 286 | 49 077 | 40 969 | 30 | 93 | 32.5 | 4 029 | 43 286 | 49 077 | | | | | | |
| Unit 2 | 3 911 | 99 % | 30 | 67 | 26.5 | 3 291 | 48 773 | 55 299 | 46 163 | 30 | 67 | 26.5 | 3 291 | 48 773 | 55 299 | | | | | | |
| Unit 3 | 2 857 | 88 % | 30 | 44 | 22.0 | 2 726 | 62 168 | 70 487 | 58 841 | 30 | 44 | 22.0 | 2 726 | 62 168 | 70 487 | | | | | | |
| Unit 4 | 1 927 | 97 % | 30 | 33 | 17.4 | 2 153 | 65 527 | 74 295 | 62 020 | 30 | 33 | 17.4 | 2 153 | 65 527 | 74 295 | | | | | | |
| Unit 5 | 1 646 | 99 % | 30 | 28 | 15.8 | 1 958 | 68 876 | 78 091 | 65 189 | 30 | 28 | 15.8 | 1 958 | 68 876 | 78 091 | | | | | | |
| Unit 6 | 1 388 | 82 % | 30 | 20 | 14.3 | 1 768 | 89 299 | 101 247 | 84 519 | 30 | 20 | 14.3 | 1 768 | 89 299 | 101 247 | | | | | | |
| Assuming Base Case Dust at 200mg/Nm ³ | | | | | | | | | | | | | | | | | | | | | |
| Base Case in 2006 | | | | | Advanced Tertiary Secondary Cyclones (ATSC) | | | | | Electrostatic Precipitator 3-Fields (ESP-3) | | | | | Electrostatic Precipitator 4-Fields (ESP-4) | | | | | | |
| | | | | | Efficiency | ACC | Fixed OP | Variable OP | Outlet dust | Efficiency | ACC | Fixed OP | Variable OP | Outlet dust | | | | | | | |
| | | | | | % | % | %TEC/yr | %TEC/yr | mg/Nm ³ | % | % | %TEC/yr | %TEC/yr | mg/Nm ³ | | | | | | | |
| | | | 70 % | 7.4 % | 4 % | 1 % | 100 | 1 % | 100 | 85 % | 7.4 % | 4 % | 1 % | 50 | | | | | | | |
| | Design Feed | Utilisation | Actual Feed | Outlet Dust | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ATSC | Cost-Effectiveness: Base to ATSC | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ESP-3 | Cost-Effectiveness: Base to ESP-3 | Incremental Cost-Effectiveness: ATSC to ESP-3 | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ESP-4 | Cost-Effectiveness: Base to ESP-4 | Incremental Cost-Effectiveness: ESP-3 to ESP-4 |
| | kt/y | % | kt/y | mg/Nm ³ | mg/Nm ³ | t/y | ME | k€/y | €/tDust | mg/Nm ³ | t/y | ME | k€/y | €/tDust | €/tDust | mg/Nm ³ | t/y | ME | k€/y | €/tDust | €/tDust |
| Unit 1 | 5 480 | 97 % | 5 319 | 200 | 100 | 133 | 8.8 | 1 094 | 8 228 | 50 | 199 | 22.0 | 2 724 | 13 656 | 24 513 | 30 | 226 | 32.5 | 4 029 | 17 824 | 49 077 |
| Unit 2 | 3 911 | 99 % | 3 856 | 200 | 100 | 96 | 7.2 | 894 | 9 271 | 50 | 145 | 17.9 | 2 225 | 15 388 | 27 621 | 30 | 164 | 26.5 | 3 291 | 20 083 | 55 299 |
| Unit 3 | 2 857 | 88 % | 2 506 | 200 | 100 | 63 | 6.0 | 740 | 11 817 | 50 | 94 | 14.9 | 1 843 | 19 614 | 35 207 | 30 | 106 | 22.0 | 2 726 | 25 599 | 70 487 |
| Unit 4 | 1 927 | 97 % | 1 877 | 200 | 100 | 47 | 4.7 | 585 | 12 456 | 50 | 70 | 11.7 | 1 455 | 20 673 | 37 109 | 30 | 80 | 17.4 | 2 153 | 26 982 | 74 295 |
| Unit 5 | 1 646 | 99 % | 1 625 | 200 | 100 | 41 | 4.3 | 532 | 13 092 | 50 | 61 | 10.7 | 1 324 | 21 730 | 39 005 | 30 | 69 | 15.8 | 1 958 | 28 361 | 78 091 |
| Unit 6 | 1 388 | 82 % | 1 131 | 200 | 100 | 28 | 3.9 | 480 | 16 974 | 50 | 42 | 9.6 | 1 195 | 28 173 | 50 571 | 30 | 48 | 14.3 | 1 768 | 36 770 | 101 247 |
| Assuming Base Case Dust at 250mg/Nm ³ | | | | | | | | | | | | | | | | | | | | | |
| Base Case in 2006 | | | | | Advanced Tertiary Secondary Cyclones (ATSC) | | | | | Electrostatic Precipitator 3-Fields (ESP-3) | | | | | Electrostatic Precipitator 4-Fields (ESP-4) | | | | | | |
| | | | | | Efficiency | ACC | Fixed OP | Variable OP | Outlet dust | Efficiency | ACC | Fixed OP | Variable OP | Outlet dust | | | | | | | |
| | | | | | % | % | %TEC/yr | %TEC/yr | mg/Nm ³ | % | % | %TEC/yr | %TEC/yr | mg/Nm ³ | | | | | | | |
| | | | 70 % | 7.4 % | 4 % | 1 % | 100 | 1 % | 100 | 85 % | 7.4 % | 4 % | 1 % | 50 | | | | | | | |
| | Design Feed | Utilisation | Actual Feed | Outlet Dust | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ATSC | Cost-Effectiveness: Base to ATSC | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ESP-3 | Cost-Effectiveness: Base to ESP-3 | Incremental Cost-Effectiveness: ATSC to ESP-3 | Outlet Dust | Dust Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to ESP-4 | Cost-Effectiveness: Base to ESP-4 | Incremental Cost-Effectiveness: ESP-3 to ESP-4 |
| | kt/y | % | kt/y | mg/Nm ³ | mg/Nm ³ | t/y | ME | k€/y | €/tDust | mg/Nm ³ | t/y | ME | k€/y | €/tDust | €/tDust | mg/Nm ³ | t/y | ME | k€/y | €/tDust | €/tDust |
| Unit 1 | 5 480 | 97 % | 5 319 | 250 | 100 | 199 | 8.8 | 1,094 | 5 485 | 50 | 266 | 22.0 | 2 724 | 10 242 | 24 513 | 30 | 293 | 32.5 | 4 029 | 13 773 | 49 077 |
| Unit 2 | 3 911 | 99 % | 3 856 | 250 | 100 | 145 | 7.2 | 894 | 6 181 | 50 | 193 | 17.9 | 2 225 | 11 541 | 27 621 | 30 | 212 | 26.5 | 3 291 | 15 519 | 55 299 |
| Unit 3 | 2 857 | 88 % | 2 506 | 250 | 100 | 94 | 6.0 | 740 | 7 878 | 50 | 125 | 14.9 | 1 843 | 14 710 | 35 207 | 30 | 138 | 22.0 | 2 726 | 19 781 | 70 487 |
| Unit 4 | 1 927 | 97 % | 1 877 | 250 | 100 | 70 | 4.7 | 585 | 8 304 | 50 | 94 | 11.7 | 1 455 | 15 505 | 37 109 | 30 | 103 | 17.4 | 2 153 | 20 850 | 74 295 |
| Unit 5 | 1 646 | 99 % | 1 625 | 250 | 100 | 61 | 4.3 | 532 | 8 728 | 50 | 81 | 10.7 | 1 324 | 16 297 | 39 005 | 30 | 89 | 15.8 | 1 958 | 21 915 | 78 091 |
| Unit 6 | 1 388 | 82 % | 1 131 | 250 | 100 | 42 | 3.9 | 480 | 11 316 | 50 | 57 | 9.6 | 1 195 | 21 130 | 50 571 | 30 | 62 | 14.3 | 1 768 | 28 413 | 101 247 |

Source: CONCAWE 6/11

Driving force for implementation

Reduction of particulate emissions.

Example plants

Within the 61 sites of the TWG sample, 17 of 22 FCC European refineries use ESPs in their FCC unit. They are also used in many refineries in the US and Japan. As an example, TOTAL in Spergau has an ESP operated on a FCC unit receiving deeply hydrotreated feedstocks.

Reference literature

[28, Tebert et al.2009], [130, Reza Sadeghbeigi 2012], [139, CONCAWE 6/11 2011], [143, Oekopol 2012], [151, Sema, Sofres 1991], [166, CONCAWE 1999], [167, VDI 2000], [185, Pernis 1999], [191, UBA Austria 1998], [207, TWG 2001], [221, Italy 2000], [Questionnaire 18].

4.5.5.3 Other filters

Description

A further option for regenerator exhaust gases are bag or fabric filters, and ceramic or stainless steel filters (for bag filters, see additional information in Section 4.23.4.3).

Reverse flow (blowback) ceramic or sintered metal filters are devices where, after retaining the solids elements at the surface as a cake, they are dislodged by initiating a reverse flow. The dislodged solids are then purged from the filter system.

Achieved environmental benefits

Reverse flow (blowback) and fabric filters are both able to achieve higher performance figures (1 – 10 mg/Nm³) than cyclones and electrostatic precipitators. Furthermore, in the case of ceramic filters, they prove to be particularly efficient for retaining the finest particulates, and to cope with start-up or upset conditions.

Cross-media effects

None identified so far, except for the need for elimination or valorisation of the collected dust, which is an issue for all dry filters.

Operational data

Bag or fabric filters are temperature sensitive (<200 – 240 °C) and hence their use is limited. They can also cause a significant pressure drop, which has to be taken into account in order to fit the overall process.

On the other hand, reverse flow (blowback) ceramic filters are more sophisticated systems which have proven to be appropriate for this application. One of them, installed since mid-2004 as a full third-stage filter on a 2 100 t/day RCC unit, has operated without incident since its start-up. Blowback sequences are triggered in function of the progressive build-up of the pressure drop generated by the filter, which is an important parameter to monitor. The filter system achieved a steady-state recovery pressure differential after approximately 100 blowback cycles (i.e. nearly one month) and the operating pressure drop due to the filter has been low enough to avoid any adverse impacts on the RCC operation. The related environmental performance is much better than any other filtration processes applied to FCC. As shown in Figure 4.18, the PM concentration measured by opacity analysis has always been below 5 mg/Nm³ since the filter commissioning, and the typical filter performance is 1 – 2 mg/Nm³.

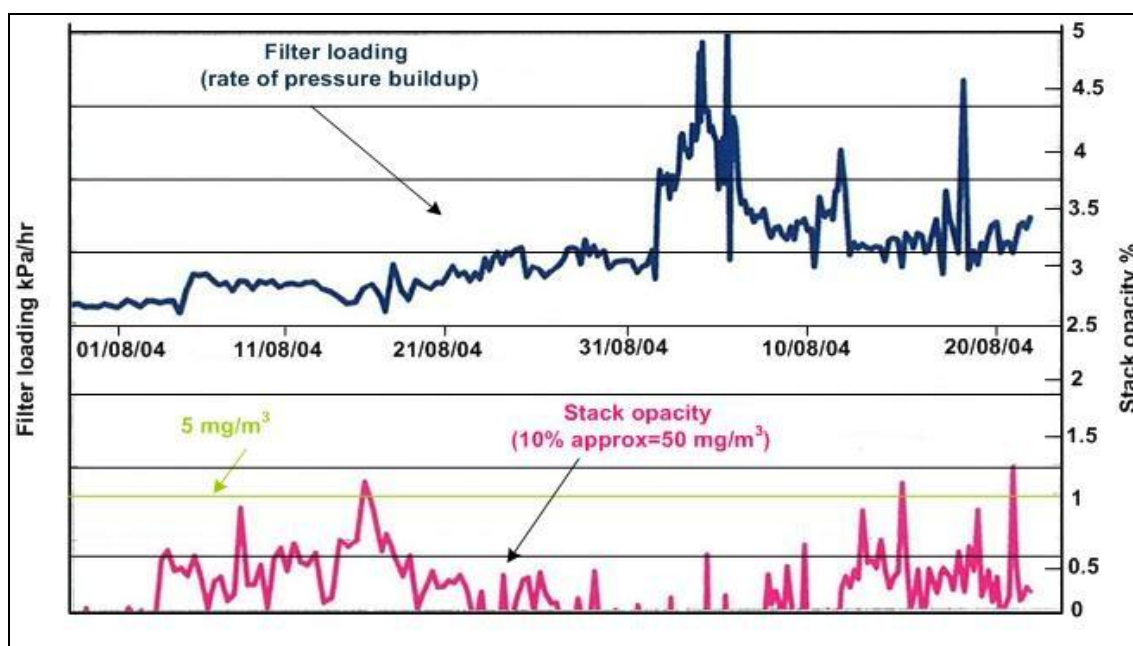


Figure 4.18: Performance of a FCC sinter alloy third-stage blowback filter

However, besides the filter pressure drop, other variables have to be monitored in order to ensure a stable filter functioning, such as valve operating and closing times, flue-gas temperatures, blowback accumulation pressure and blowback gas temperature.

Recent data provided for a full stream third-stage blowback filter (stainless steel made) operated at a FCC unit (1.1 Mt/y) at BAZAN (ORL) refinery in Haifa (Israel) show that PM emissions comply with the 20 mg/Nm³ emission standard and usually allow concentrations well below 15 mg/Nm³ [144, COM 2012].

Applicability

Bag or fabric filters can be retrofitted to the underflow of three-stage cyclones. However, they are not favoured for use in the FCC because of the pressure drop, the potential for ‘blinding’ of the bags, the large space required and their inability to cope with upset conditions.

On the other hand, third-stage ceramic filters have proven to be applicable to catalytic cracking flue-gas cleaning since 2004. They are even successful in their ability to cope with various FCC upset conditions. Two specific cases have been reported in the available literature so far. The first one is the handling of upstream concentrations of up to 20 000 mg/Nm³ during a two-week catalyst attrition problem, with a solid load increase from 250 kg/day to 1 000 – 2 000 kg/day, allowing the RCC unit to keep complying with applicable emission standards and avoid shutdown. The second one is the safe operation of such a filter during torch oil firing in the regenerator, in order to maintain its temperature during emptying and urgent repairs. Therefore, it is also possible to benefit from the ceramic filter system during start-up and shutdown, which corresponds to a major improvement compared with ESPs. Scaleup to full regenerator flow from more commonly sized European FCC units needs to be clearly demonstrated.

Economics

The specific investment cost for blowback ceramic filters will depend on the temperature and the stream capacity. The cost for a third-stage (full stream) filter is estimated at USD 80/m³/h for temperatures below 450 °C, and USD 210/m³/h for higher temperatures up to 750 °C. For smaller hot filters concerned in four-stage application, this cost is about USD 260/m³/h (all costs expressed for the year 2009 and for actual flue-gas volumes). For a generic 2.4 Mt/yr FCC unit, the installed capital cost in 2009 was estimated to be EUR 15 – 20 million (USD 22 – 30 million).

Driving force for implementation

Recent reverse flow (blowback) ceramic filters are of the highest interest for FCC applications, where the magnitude of PM emissions, considered together with their associated granulometry and chemical content, is likely to raise health and environmental issues. This technique allows a high-performance filtration of catalyst PM emissions, including finest particulates and heavy metals. It has a very low sensitivity to start-up and upsets and prevents related adverse effects on dust loads, particle size, or flow rates. Its compactness is also favourable for retrofitting situations.

Example plants

Full-stream third-stage ceramic or stainless steel filters are operated in three refineries: the BP refinery in Kwinana (Australia, 2004), the BAZAN (ORL) refinery in Haifa (Israel, 2009), and another in the US (to be commissioned). Around 15 partial-stream (fourth-stage) ceramic separators and hopper filters are also operated in western Europe, North America and the Middle East.

Reference literature

[22, Glennly et al.2008], [30, Sawyer et al.2009], [144, COM 2012], [156, MCG 1991].

4.5.6 Sulphur oxides abatement techniques

4.5.6.1 SO_x-reducing catalyst additives

Description

Sulphur dioxide in the regenerator off-gas of a FCC unit can be reduced by using a metallic oxide catalyst (e.g. Al/Mg, Ce) which transfers a significant portion of the sulphur associated with the coke on the catalyst back to the reactor, where it is liberated as hydrogen sulphide. This leaves the reactor with the cracked vapour product for capture in the amine scrubbing system of the refinery and hence conversion of sulphur in the SRU.

SO_x reduction is a three-step process:

- 1) catalytic oxidation of SO₂ to SO₃ in the regenerator;
- 2) adsorption on the additive of SO₃ produced in the regenerator to give a sulphate which, on return to the reactor;
- 3) reverts to the oxide and releases hydrogen sulphide into the product gas stream for recovery.

Developed in the late 1970s, SO_x-reducing catalysts were initially alumina-based and very much subject to deactivation. Progressively, the potential for SO₃ picking-up in the regenerator was substantially increased by replacing pure alumina-based binders with magnesium-aluminate binders (1980s: 1 Al mole for 2 Mg mole) and later with hydrotalcite binders (1990s: 1 Al mole for 3 – 4 Mg mole). State-of-the-art catalysts developed since 2000 show performances improved by 35 – 80 % compared with the first hydrotalcite binder compounds. Pick-up factors (PUF – kg SO₂ removed per kg additive introduced) of up to 20 can now theoretically be reached.

Achieved environmental benefits

The amount of SO_x removed is strongly dependent on the SO_x raw concentration in the regenerator, the amount of SO_x-reducing additive added to the unit, and on the type and efficiency of the SO_x-reducing additive itself. Some available test data also show that the removal performance is highly influenced by the current oxygen concentration and by the additive's own resistance to attrition in the operating conditions prevailing in the particular plant concerned.

In the full combustion mode, removal efficiencies achieved with state-of-the-art additives are typically >60 %. Even higher removal rates (of up to 95 – 99 %) have been reported in commercial operation. Best performances are associated to the most favourable operating conditions, in particular lowest raw sulphur concentrations in the regenerator and optimisation of the regenerator and other process variables.

In the partial combustion mode, the typical reduction might be lower than in full combustion mode and, in most cases, more additive is required. Specific partial-burn additives have recently been developed, and have shown to be twice as active as the older additives. State-of-the-art additives are now typically able to remove >50 % of emitted SO_x, and even higher reductions (up to 90 – 95 %) have been reported in commercial operation. Here again, best performances are associated with the most favourable operating conditions, as above, in particular the lowest raw sulphur concentrations, lowest proportions of pre-existing reduced species (COS, H₂S) in the regenerator before the CO boiler, and the longest regenerator residence times as shown graphically in Figure 4.19. Nevertheless, in some units with specific unfavourable conditions, the maximum SO_x removal may still be 30 – 35 %.

However, the higher the removal rate, the lower the pick-up factor observed.

- In one example, the literature [25, Pham et al.2009] reports a case where an 85 % reduction in SO_x, resulting in a 50 ppmv residual emission (0 % O₂), could be achieved with a PUF of 18 kg SO_x removed per kg of additive incorporated. A further reduction of emissions to below 25 ppmv (0 % O₂) decreased the PUF to 14 kg SO_x removed per kg of additive. The concentration required to reduce emissions below 25 ppmv was in the order of 5 % w/w of the total catalyst inventory. The relative cost increase from 50 to 25 ppm was 31 %.
- A second example is described in detail as the case study n°1 for a short trial performed on a ‘deep’ partial-burn FCC with 7–8 mol % CO in the regenerator [57, Roberts et al.2009]. It shows a relatively acceptable efficiency for achieving up to 30 – 35 % SO_x removal with a PUF >10. However, it confirms that an attempt to reach 50 % SO_x removal in such unfavourable conditions was technically and economically almost impossible, as the PUF fell below five and the additional energy consumption at constant steam production was increasing by >8 %, leading to specific costs above EUR 10k/tonne SO₂ saved.

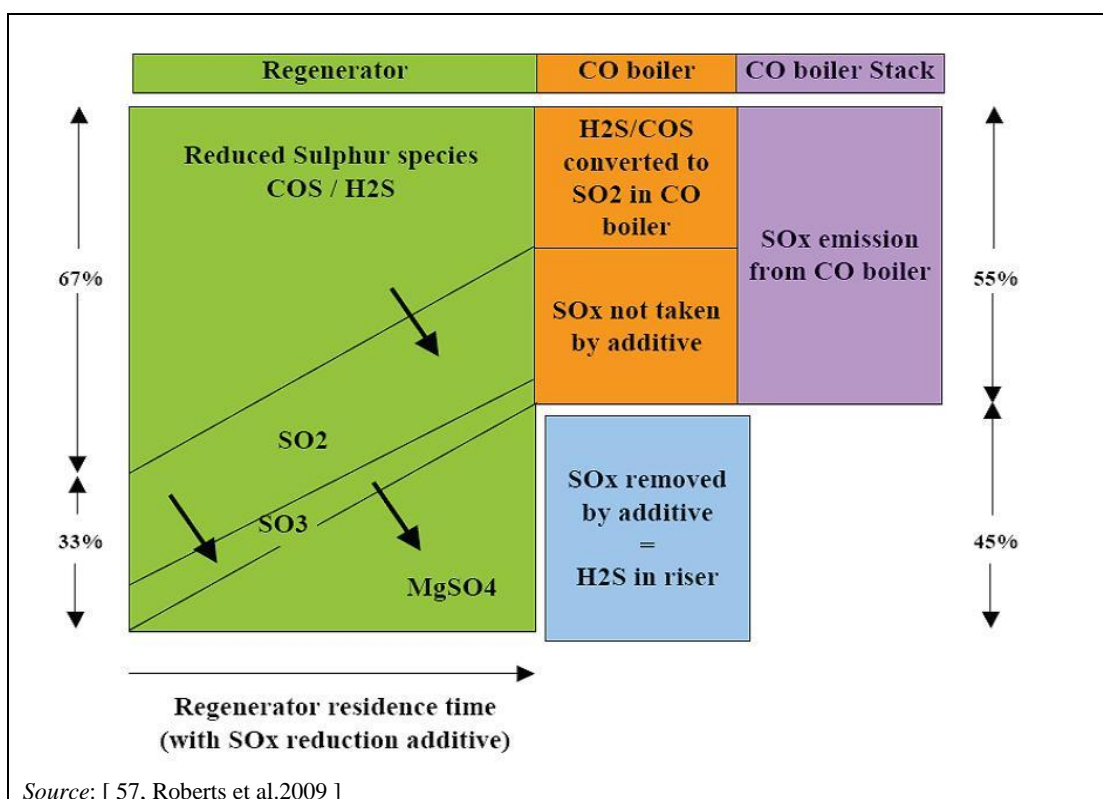


Figure 4.19: Graphical representation of the influence of SO_x -reducing additives in a partial-burn FCC unit for a given initial concentration profile

Cross-media effects

Disadvantages of this technique include the following:

- SO_x -reducing additive is not really a polyvalent technique implementable to all units as, despite recent progress made, it actually remains more efficient and economically more attractive in the full combustion mode.
- There is a possibility of poorer yield of products from FCC units and reduced FCC unit operating flexibility, especially when additives are applied at very high rates (>10 – 15 % of fresh catalyst addition).
- SO_x -reducing additives might have a detrimental effect on PM by increasing catalyst losses due to attrition, and on NO_x generation by participating in the CO promotion activity. When used in partial-burn mode, this can lead to significant increases in the supporting fuel consumption in the CO boiler for an equivalent steam production.
- Other impacts are additional waste generation, and the possibility of bottlenecks in the H_2S amine treating facilities.

Operational data

For an initial concentration of up to $4\,000 - 4\,500 \text{ mg/Nm}^3$ (corresponding to a feedstock sulphur content of around 2 – 2.5 %), a typical downstream effluent of a FCC unit using this technique has a SO_2 concentration of $1\,000 - 3\,000 \text{ mg/Nm}^3$ at 3 % O_2 , depending on the additive usage rate and the unit combustion mode.

Figure 4.20 and Figure 4.21 below relate to a full combustion FCC unit, operated under rather unfavourable conditions due to a very low inventory replacement rate (daily additions of only 0.5 % of the unit inventory), together with respective average rises and regenerator temperatures of 508°C and 673°C . The two given sets of data illustrate the results achieved in the case of a high average sulphur content (1.6 %) and a low one (0.5 %), for which the removal yield is higher.

These two graphs show the profile of the additives' performance over time (expressed as days on the X-axis) for two different types of feedstock (high and low sulphur).

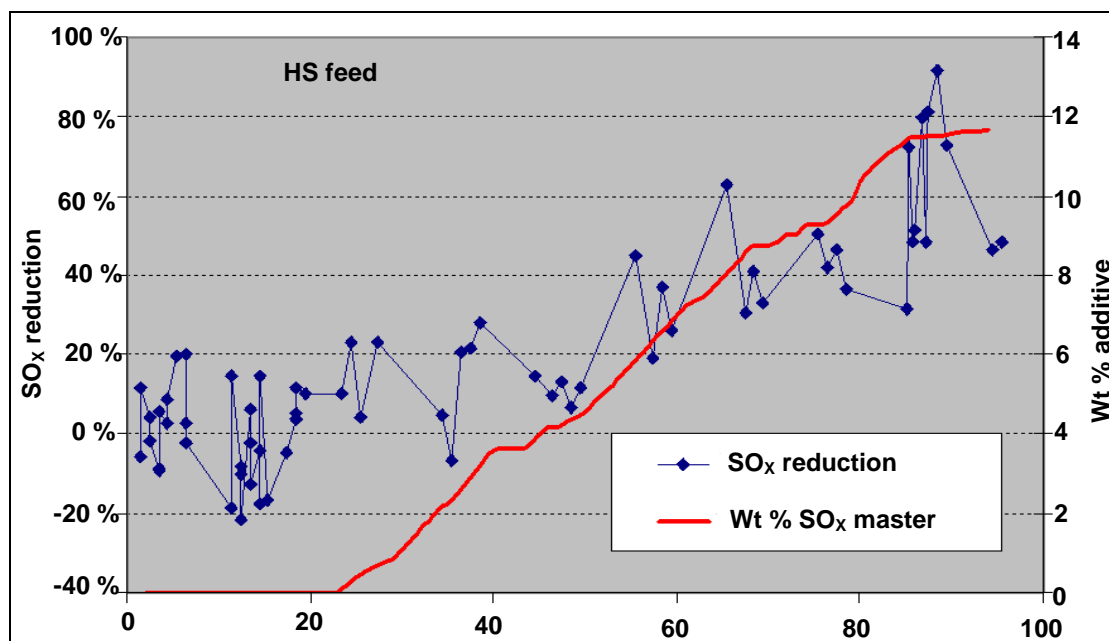


Figure 4.20: SO_x-reducing additives' performance with a 1.6 % sulphur FCC unit feedstock

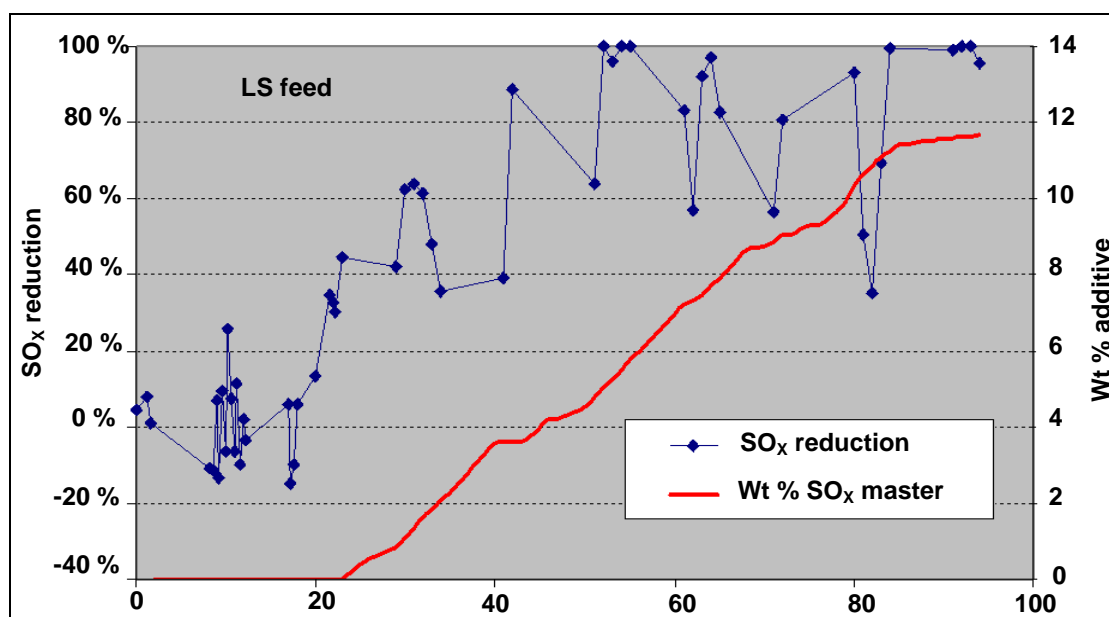


Figure 4.21: SO_x-reducing additive's performance with a 0.5 % sulphur FCC unit feedstock

These results are consistent with those reported by a European site, as illustrated in Figure 4.22, where a 50 % abatement (average concentration from 980 to 450 mg/Nm³ at 3 % O₂) has been achieved since 2009 on a 1.5 Mt/yr FCC with a 0.32–0.45 % S feedstock [Questionnaire N°15].

For an additive content of only 3 % in the catalyst inventory, a 25 % reduction of SO₂ emissions is reported even with a typical feed sulphur content of 0.6–1.8 % [Questionnaire N°50]. The SO_x removal ability of state-of-the-art SO_x-reducing additives is determined by the amount in the catalyst inventory rather than by the daily addition rate, showing an increased stability.

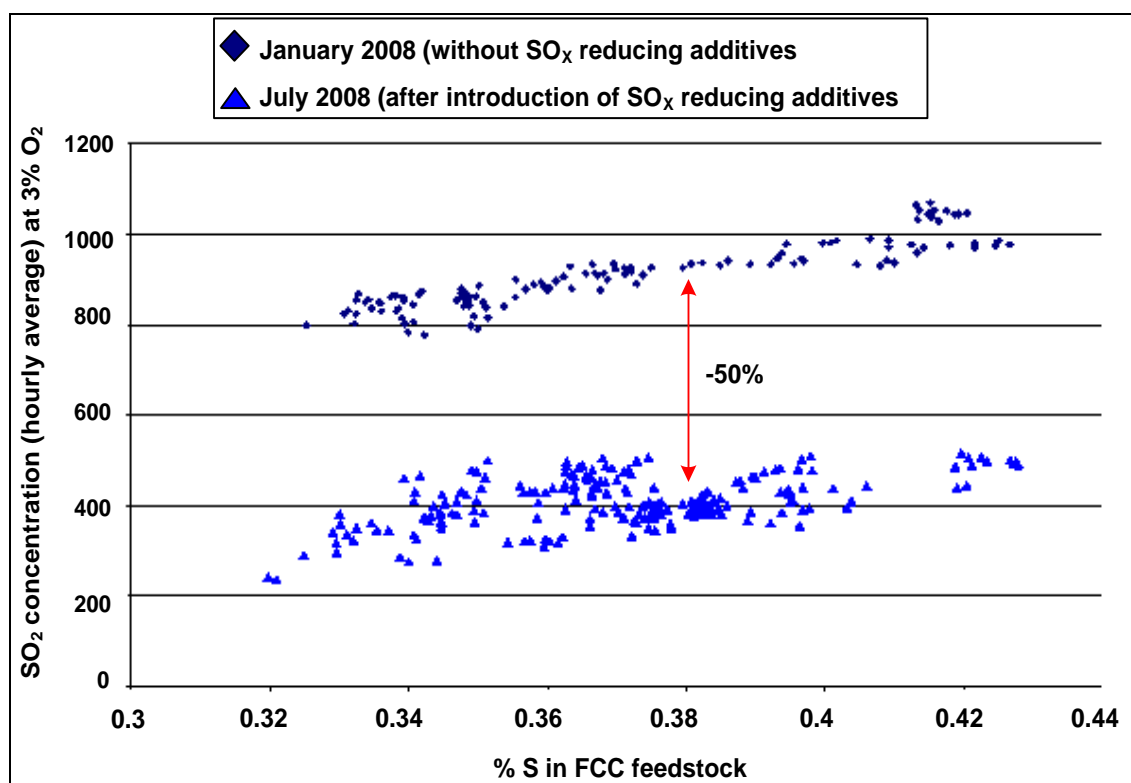


Figure 4.22: SO₂ emissions decrease from a French FCC unit using SO_x-reducing additives

Applicability

The outlet SO_x concentration achievable with this technique is highly dependent on the SO_x inlet concentration, the amount of additive that can be used, and the unit operation mode.

This technique is sensitive to unit design, especially regenerator conditions. It operates most effectively under full combustion mode conditions, where virtually all the sulphur in the flue-gases can be removed when the technique can be retrofitted in the most favourable conditions.

FCC unit performance may, however, be affected and the transfer catalyst replacement rate may be significant. A fine retuning of the catalyst system might be required in the case of large quantities of additives being incorporated.

Thanks to its high adjustability, this technique can also be combined together with other process-related or end-of-pipe abatement techniques.

- In association with wet scrubbing, as has been the case since 2006 for a BP refinery in Texas City, where additives help to reduce the operating chemical consumption (e.g. caustic) and energy (e.g. pumping). Another example of this is reported for a Middle Eastern refinery which processes 30 000 barrels per day (around 2 million t/yr) of a 100 % atmospheric residue feedstock with a high sulphur content of 2.7 % operated in full combustion, where it has been decided to use such an additive in order to master corrosion problems due to high inlet SO_x concentrations in an existing scrubber. In this refinery a 15 % reduction of the scrubber operating cost has been observed, exceeding the cost for the SO_x-reducing additive, which was fully covered [26, Kramer et al.2009].
- In association with high-efficiency filters, the two techniques could lead to very cost-effective conditions [30, Sawyer et al.2009].
- In order to increase flexibility in the choice of the feed quality (e.g. external inputs), or for decreasing the severity of the upstream feed hydrotreatment.

On the other hand, this technique proves to be less efficient for FCC units operated in deep partial combustion modes, at high regenerator temperatures, with low daily replacement rates, or for which very low SO_x outlet concentrations are required. In North America, SO_x -reducing catalysts are being used preferably with wet scrubbing for FCC units in refineries with capacities lower than 150 000 barrels/day (8 Mt/yr).

Economics

There is no major investment cost required: only minor capital expenses are needed for the dosing equipment for introducing the additive to the catalyst system. As an example, the cost reported for a European site is EUR 300 000 including foundation, construction, piping, downstream capacity improvement, and the permit.

Operating expenses are dependent on the unit, the initial SO_2 emissions and the SO_2 target. The cost reported by a European site, for a 264 kg/day injection rate and a 94 t/yr additional waste elimination of spent catalyst is EUR 1.3 million/yr.

Potential investment and operational costs for implementing this technology on two FCC units in the Colorado refineries (US) were estimated in 2005. Data extrapolated to 2007 give USD 500 per tonne per year of SO_2 saved, assuming a resulting SO_2 emission decrease of only 35 – 50 %. [17, Jeavons and Francis 2008]. These data are rather consistent with costs reported more recently by other US sources, also for 2007, according to which the cost for obtaining 25 ppmv at 0 % O_2 (yearly average) and 50 ppmv at 0 % O_2 (7-day rolling average) is in the range of USD 500 – 880 per tonne of SO_2 removed.

Another cost estimation is given in Figure 4.23, based on a major catalyst manufacturer's field experience within US refineries. The graph is provided for a reference unit of 50 000 barrels/day (around 3 million t/yr) capacity, with a 150-tonne catalyst inventory. The range reflects a wide variety of FCC unit configurations, with different untreated off-gas SO_x levels, feed types and regenerator operational conditions (including full and partial combustion). [25, Pham et al.2009]

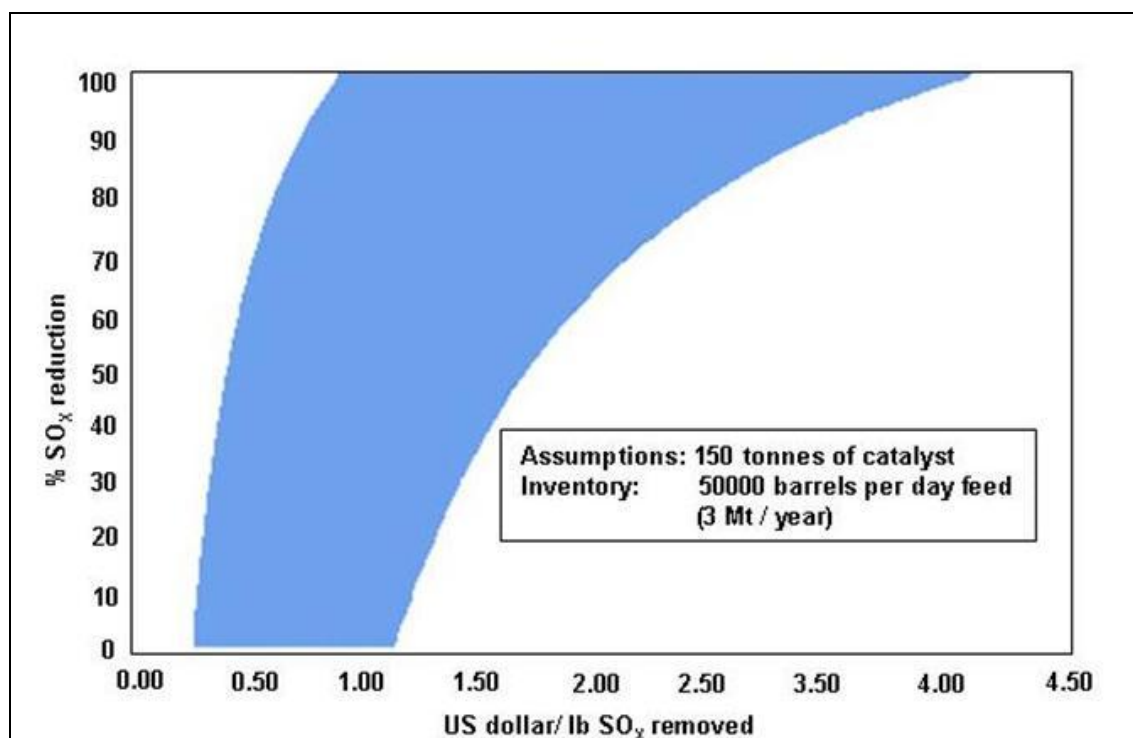


Figure 4.23: FCC SO_x reduction additives' specific cost versus SO_x overall reduction target

A similar approach has been followed which proposes a cost estimation for full and partial combustion mode, as drawn from the European catalyst market. [280, ALBERMARLE 2008]

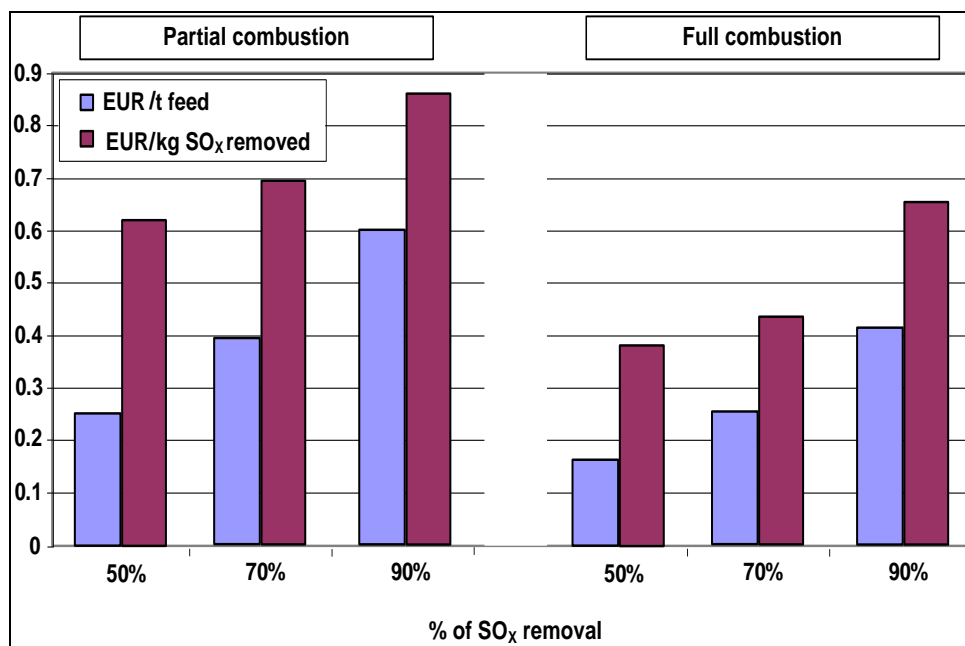


Figure 4.24: Economics of SO_x reduction additives for FCC units - general cost overview

Finally, the available literature also reports the following removal costs reached during particular trials aiming at ultra-low SO₂ emissions, as shown in Table 4.23 below [30, Sawyer et al. 2009].

Table 4.23: Performance and specific removal costs with SO_x-reducing additives at a high injection rate

| | Refinery A | Refinery B |
|--|------------|------------|
| Fresh feed rate (t/day) | 2 876 | 6 847 |
| Fresh feed (API) | 24.9 | 28.5 |
| Uncontrolled SO ₂ (ppmv) | 178 | 326 |
| Controlled SO ₂ (ppmv) | 10 | 7 |
| SO ₂ reduction (%) | 95 | 98 |
| Removal cost ⁽¹⁾ (EUR/t SO ₂) | 780 | 940 |

⁽¹⁾ Respectively USD 0.51 and 0.61 per lb of SO₂ (2009 value).

Table 4.24: Economics of two sulphur abatement techniques: additives and wet gas scrubber – Cost-effectiveness data from a sample of 6 FCC units

| Base case in 2006 | | | | | Sulphur reduction additives (SRA) | | | | | Wet gas scrubber (WGS) | | | | | |
|-------------------|-------------|-------------|-------------|------------------------|-----------------------------------|-------------------------------------|--------------------------------|------------------------------|---------------------------------|------------------------|-------------------------------------|--------------------------------|------------------------------|---------------------------------|--|
| | | | | | Efficiency | ACC | Fixed OP | | Variable OP | Efficiency | ACC | Fixed OP | | Variable OP | |
| | | | | | 40 % | 7.4 % | 4 % TEC/yr | | 1000 €/t SO ₂ | 90 % | 7.4 % | 4 % TEC/yr | | 0.93 €/tFF | |
| Unit | Design Feed | Utilisation | Actual Feed | Outlet SO ₂ | Outlet SO ₂ | SO ₂ Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SRA | Cost-Effectiveness: Base to SRA | Outlet SO ₂ | SO ₂ Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to WGS | Cost-Effectiveness: Base to WGS | Incremental Cost-Effectiveness: SRA to WGS |
| | kt/yr | % | kt/yr | mg/Nm ³ | mg/Nm ³ | t/yr | M€ | k€/yr | €/t SO ₂ | mg/Nm ³ | t/yr | M€ | k€/yr | €/t SO ₂ | €/t SO ₂ |
| 1 | 5 480 | 97 % | 5 319 | 3 134 | 1 880 | 3 334 | 0.9 | 3 439 | 1 031 | 313 | 7 502 | 49.4 | 10 582 | 1 410 | 1 714 |
| 2 | 1 591 | 85 % | 1 351 | 3 012 | 1 807 | 814 | 0.4 | 863 | 1 061 | 301 | 1 831 | 23.5 | 3 940 | 2 152 | 3 024 |
| 3 | 2 857 | 88 % | 2 506 | 1 504 | 902 | 754 | 0.6 | 824 | 1 094 | 150 | 1 695 | 33.4 | 6 143 | 3 623 | 5 647 |
| 4 | 1 999 | 79 % | 1 577 | 1 486 | 892 | 469 | 0.5 | 526 | 1 122 | 149 | 1 055 | 27.0 | 4 543 | 4 307 | 6 856 |
| 5 | 1 648 | 99 % | 1 625 | 860 | 516 | 279 | 0.4 | 330 | 1 181 | 86 | 629 | 24.0 | 4 250 | 6 758 | 11 220 |
| 6 | 1 927 | 97 % | 1 877 | 362 | 217 | 136 | 0.5 | 192 | 1 410 | 36 | 306 | 26.4 | 4 756 | 15 543 | 26 850 |

Source: [139, CONCAWE 6/11 2011]

Driving force for implementation

Reduction of sulphur oxide emissions from the FCC.

Example plant(s)

More than 60 refineries worldwide are applying SO_x reduction additives to the catalyst, including several partial-combustion units in Germany, Japan, and South Africa. The method is well established commercially.

Reference literature

[25, Pham et al.2008], [26, Kramer et al.2009], [30, Sawyer et al.2009], [36, CONCAWE n°4/09 2009], [57, Roberts et al.2009], [139, CONCAWE 6/11 2011], [151, Sema, Sofres 1991], [163, FWE 1999], [166, CONCAWE 1999], [221, Italy 2000], [228, TWG 2000], [280, ALBERMARLE 2008], [Questionnaires n° 15, 27, 49, 50].

4.5.6.2 Wet scrubbing

Description

There are several wet scrubbing processes. A brief description of them is included in Section 4.23.5.4. The types of wet scrubbing that are typically used for FCC units are:

- sodium- or magnesium-based non-regenerative wet scrubbing, using packed towers, plate towers, spray chambers, or Venturi systems;
- those combining conventional scrubbing techniques with the use of a regenerative process (e.g. the LABSORBTM produced by BELCO using a patented solution containing soda and phosphoric acid or CANSOLV process with an amine solution – see Section 4.23.5.2.3).

Two Venturi systems have been successfully developed by ExxonMobil specifically for FCC application:

- The Jet Ejector Venturi (JEV) scrubber, for lower pressure streams, where the absorbing liquid is sprayed into the flue-gas stream at the inlet of the Venturi above the ‘throat’. Gas and liquid then pass through the throat under conditions of high turbulence.
- The High Energy Venturi (HEV) scrubber, for higher pressure streams, which use the kinetic energy of the flue-gas to break the absorption liquid into droplets. This technique requires a greater drop in gas pressure but it has higher efficiencies for small particulates compared to Jet Ejector Venturi scrubbers, in particular for PM₁₀ and PM_{2.5}, and is typically able to remove PM₂.

Another successful system worth mentioning is the Electro-dynamic Venturi (EDV®) developed by BELCO, which combines the techniques used in Venturi scrubbers with electrostatic dust separation. The system houses a spray tower along with forced condensation and water-spraying filtering modules and droplet separators. It can be associated, like in the ENI Sannazzaro refinery, with the LABSORBTM regenerative process (see Section 4.23.4.4), or also with the LoTOXTM deNO_x SNERT process using ozone injection (see Sections 4.5.4.5 and 4.23.3.1).

Achieved environmental benefits

Even if SO₂ removal is the first objective, a suitably designed wet scrubbing process will normally provide a very high removal efficiency of both SO₂ and particulates, taking into account that SO₃ abatement is typically not as high as SO₂. With the inclusion of an extra treatment tower to oxidise the NO to NO₂, NO_x can also be removed efficiently. Table 4.25 shows the achievable emission levels that can be expected with a wet scrubber.

Table 4.25: Generic achievable efficiency and emission levels for wet scrubbers

| Parameter | Efficiency (%) ⁽¹⁾ | Inlet (mg/Nm ³) at 3 % O ₂ | Outlet (mg/Nm ³) at 3 % O ₂ |
|-----------------|-------------------------------|---|--|
| SO ₂ | 95 – 99.9 | 600 – 10 000 | <60 – 160 ⁽²⁾ |
| Particulates | 85 – 95 | 350 – 800 | <30 – 60 ⁽²⁾ |
| NO _x | Up to 70 | 600 | 180 |

NB: Particulates removal is very much design-related and system pressure drop is highly variable. Scrubbers are less effective at reducing submicron particles.
⁽¹⁾ Source: [45, Sabo et al. 2007]
⁽²⁾ Based on sample data of non-regenerative scrubbers as shown in Table 4.26.

In the case of regenerative scrubbing, the main additional benefit is obviously the possibility to regenerate the SO_x-absorbing reagent and to recover concentrated SO₂ streams which can be converted and sold/recycled as liquid SO₂, sulphuric acid or elemental sulphur. In correlation to this, a much lower amount of solid residue must be recovered and eliminated. Compared to a non-regenerative process, the energy consumption is also reported to be lower (see below Operational data and Economics paragraphs).

Cross-media effects

Non-regenerative wet scrubbing systems create secondary problems of aqueous slurry waste disposal and increase the refinery energy consumption. The effluent water purge contains sulphates (e.g. Na₂SO₄). Another drawback is the consumption of a significant quantity of expensive raw material (e.g. caustic soda) which is roughly proportional to inlet sulphur loadings. Flue-gas reheat may be needed to prevent plume mist.

Typical impacts of regenerative systems are the possible debottlenecking of H₂S-handling facilities (e.g. SRU, amine scrubbers), the production of other eventual by-products, as well as the need for raw material supply and handling.

Operational data

Non-regenerative scrubbing

Table 4.26 provides data observed for seven FCC units operated in the US. All of them are Venturi-type [36, CONCAWE n°4/09 2009].

Table 4.26: Wet Venturi scrubbing performances for some US FCC units

| Type | Outlet PM | Outlet PM average | % PM abatement | Inlet SO ₂ | Outlet SO ₂ | % SO ₂ abatement |
|--|-----------|-------------------|----------------|-----------------------|--------------------------|-----------------------------|
| Partial combustion with CO boiler ⁽¹⁾ | 35 – 60 | 47 | NA | NA | NA | NA |
| Partial combustion with CO boiler ⁽¹⁾ | 39 – 50 | 46 | NA | NA | NA | NA |
| Full combustion unit ⁽¹⁾ | 48 – 109 | 74 | NA | NA | NA | NA |
| Full combustion unit ⁽¹⁾ | NA | 56 | NA | NA | NA | NA |
| Partial combustion with CO boiler ⁽¹⁾ | 43 – 61 | 56 | NA | NA | NA | NA |
| Partial combustion with CO boiler ⁽²⁾ | NA | NA | NA | 425 | 61 | 90 % |
| Partial combustion with CO boiler ⁽²⁾ | NA | NA | 93 % | >1800 | 125 – 160 ⁽³⁾ | 93 % |

⁽¹⁾ Average in mg/Nm³ at 3 % O₂ (dry gas), based on spot measurements.
⁽²⁾ Daily average in mg/Nm³ at 3 % O₂ (dry gas), based on continuous emission monitoring Jet Ejector Venturi (JEV) system.
⁽³⁾ Daily average calculated from the 95th percentile range of the complete available data-set.
 NA: Not available

Regenerative scrubbing

A LABSORB™ regenerative scrubbing system has operated since 2004 at the ENI refinery in Sannazzaro (Pavia, Italy). It treats all the flue-gas (0.18 million Nm³/h – 300 °C) from the 5 500 t/day FCC unit at an inlet concentration of >1 700 mg/Nm³ (3 % O₂). Outlet gas (208 000 Nm³/h – 67°C) is released at a concentration of 50 – 250 mg/Nm³ (3 % O₂) with a SO₂ removal efficiency >85 %, as a daily average. An extra 250 kg/h concentrated SO₂ stream is sent to the SRU. Liquid waste production is 1 t/hr and solid waste production is 19 kg/h (compared to 9 t/h and 1 000 kg/h in the case of NaOH conventional absorption for the same capacity).

Another regenerative scrubbing system has been in operation since 2006 at the Valero refinery in Delaware City (Delaware, US). It includes a prescrubber, an amine-based regenerative packed bed absorber, and a caustic polisher. It is designed to treat an inlet flow of 0.75 million Nm³/h with a SO₂ removal rate of >97 %. Since its installation, it has continuously achieved 1 – 2 ppmv SO₂ at 0 % O₂ (i.e. 3 – 6 mg/Nm³ at 3 % O₂) [25, Pham et al.2009].

Table 4.27 gives the typical performance achieved with a Wellman-Lord regenerative scrubber.

Table 4.27: Typical performance achievable with a Wellman-Lord regenerative scrubber

| Technique | SO ₂ Reduction efficiency (%) | Inlet SO ₂ concentration (mg/Nm ³) at 3 % O ₂ 160 – 180 °C | Outlet SO ₂ concentration (mg/Nm ³) at 3 % O ₂ 120 °C |
|--------------|--|--|---|
| Wellman-Lord | 98 | 2 000 – 7 000 | 100 – 700 |

More information and comparison with other techniques can be found in Section 4.23.5.4.

Applicability

Wet gas scrubbers are generally recognised as flexible and reliable. Day-to-day operating changes can be readily handled. They generate a low pressure drop and operate at low temperatures. Their performance can be affected by deposition problems occurring in the course of a typical five-year run: the amount of deposition depends on the inlet catalyst and SO₂ load to the scrubber, the quality of the make-up water, the operating pH of the scrubber, and the level of purge applied to the scrubbing slurry. The deposits are formed by catalyst dust that settles at low points and by mist eliminators and hard deposits (e.g. salts of calcium) that precipitate as the operating pH is increased to achieve high SO₂ removal efficiency. Some CO₂ can be removed as well by wet scrubbers, however, in that case, it reduces the capability of the media to dissolve SO₂. These systems, in particular when using Venturi scrubbers, are also rather compact: the necessary plot spaces range from 93 m² to 465 m² for FCC capacities from 1.5 to 7.5 Mt/yr. More information can be found in Section 4.23.5.4.

The applicability may be limited in arid areas and if the by-products from treatment cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability.

Economics

Table 4.28 provides an indicative order of retrofitting costs for various FCC wet gas scrubber applications.

Table 4.28: Retrofitting costs for FCC wet gas scrubber applications

| Objective of the process | FCC capacity (Mt/yr) | Investment expenses (EUR million) | Operating expenses (EUR million/yr) |
|---|----------------------|-----------------------------------|-------------------------------------|
| SO ₂ and particulate reduction | 2.4 | 17 – 40 ⁽¹⁾ | 3.5 – 4.2 ⁽¹⁾ |
| ⁽¹⁾ Respectively, USD million 25 – 60 and 5 – 6 in 2009. Capital costs will vary considerably from location to location depending on the scrubber type and the need to upgrade infrastructure and WWTP facilities. | | | |

Additional information for the comparison of cost data for the use of sulphur reduction additives and wet gas scrubber are available in Table 4.24 in the previous section.

Non-regenerative scrubbers

The 2003 estimated costs for the installation of non-regenerative wet scrubbers in six different refineries were quoted in a 2009 prospective report from the South Coast Air Quality Management District (California, US). Investment costs cover all production and installation expenses within the scrubber battery area. It does not include foundations, external main ductworks to the scrubber inlet, or external piping and electrical supply equipment which may add 30 – 50 % to the above costs. Results of this estimation are displayed in Table 4.29.

Table 4.29: FCC unit - Cost estimates for various off-gas non-regenerative wet scrubbers

| Refinery | Off-gas flow rate (million Nm ³ /h) | Capital investment ^(*) (USD million) | Operating expenses (USD million/yr) |
|---|--|---|-------------------------------------|
| # 1 | 0.04 – 0.16 | 10 | 0.37 |
| # 2 | 0.34 – 0.36 | 13.8 | 0.56 |
| # 3 | 0.16 | 10 | 0.36 |
| # 4 | 0.37 – 0.47 | 15 | 0.57 |
| # 5 | 0.20 – 0.23 | 12.23 | 0.39 |
| # 6 | 0.15 | 9.5 | 0.32 |
| ^(*) Investment expenses cover the costs for all design, fabrication, supply, installation of the complete system, including its new stack, associated purge treatment unit, and internal piping and electrical supply equipment within the scrubber battery area. All costs at 2003 value. | | | |

With regard to the assumption of a 25-year life for the scrubber, and considering a 4 % annual increase rate, this report gives an overall cost-effectiveness average for these six plants at USD 24 600/tonne of SO₂ removed, in order to achieve at least 5 ppmv outlet concentration and 90 % abatement.

Regenerative scrubbers

A regenerative wet gas scrubber typically costs more than a non-regenerative unit to install, due to its additional complexity. One equipment supplier mentions an indicative factor of 2.4. However, the regenerative system has a significant advantage in annual operative costs because of the alkaline absorbing reagent saving and, eventually, the cost return related to by-products (e.g. elemental sulphur) sales. The annual operating costs of a regenerative system are estimated to be no more than 35 % of those of a non-regenerative system. A more detailed comparison is provided in Table 4.30.

Table 4.30: Cost comparison between regenerative and non-regenerative wet scrubbers for FCC application

| Wet scrubbing cost breakdown | Cost of a regenerative system compared with a non-regenerative system (%) |
|-----------------------------------|---|
| Capital costs | 240 |
| Operating costs: | |
| - Electrical power | 35 |
| - Steam | 10 |
| - Caustic | 18 |
| - Phosphoric acid | 5 |
| - Make-up water | <5 <35 |
| - Cooling water | <5 |
| - Water discharge and treatment | <5 |
| - Solid waste disposal | <5 |
| - Operating and maintenance staff | 20 |

Even more favourable costs have been reported in the case of the ENI Sannazzaro LABSORB unit, with a 40 % saving in total operating costs compared with a conventional wet process using caustic soda. This includes 95 % savings in absorbing solution make-up and 25 % savings in power consumption.

Driving force for implementation

Abatement of sulphur oxides and particulates from the flue-gas.

Example plants

This technique is widely used on FCC unit plants in the US. The Wellman-Lord system has been successfully applied to power plants. More information can be found in Section 4.23.5.4.

Reference literature

[25, Pham et al.2009], [30, Sawyer et al.2009], [36, CONCAWE n°4/09 2009], [45, Sabo et al.2007], [151, Sema, Sofres 1991], [183, HP 1998], [191, UBA Austria 1998], [208, Confuorto 2000].

4.5.6.3 Dry and semi-dry scrubbers

Description

Two types of scrubbing techniques exist: dry and semi-dry. The key component of the semi-dry process is a spray dryer in which the hot flue-gas comes into contact with a spray of fine droplets of lime slurry. The SO₂ is absorbed into the droplets, forming reaction products which are dried to a fine powder by the hot flue-gas. Both dry and semi-dry processes require downstream dust arrestment systems, such as an electrostatic precipitator or bag filtration. More information can be found in Section 4.23.5.4.

Achieved environmental benefits

Reduction of the SO₂ in the flue-gas. The efficiency of each process is 90 % sulphur removal with semi-dry, and about 50 % removal with dry. A dry process efficiency of 50 % is achieved with lime at relatively high temperatures (about 400 °C) when Ca/S=1, or at 130 – 140 °C when Ca/S=2. The Ca/S ratio has a major influence. With a reactant such as NaHCO₃, the abatement rate would be much higher. With lime, it is also possible to have a treatment at 900 °C in a reactor large enough to have a reasonable residence time. The abatement in this case is 80 % with CaS=2.1 and 90 % with Ca/S=3.

Cross-media effects

Deposition of solid waste results in cases where the reaction products cannot fulfil the quality needed by consumers. Other drawbacks are:

- high pressure drops across the bag filters if used;
- increased dust load in the gas stream; need for dust capture;
- operational difficulties in water/heat balance (spray dryers only);
- possibly significant pressure drops across bag filter dust arrestment plants, e.g. bag filters;
- generation of solid waste: one tonne of SO₂ reduction entails about 2.5 tonnes of solid waste being generated;
- with the dry and semi-dry scrubbers a mixture of CaSO₃, CaSO₄, fly ash and lime is produced.

Operational data

These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide, etc.

Applicability

Operates at low temperature. Waste generated can be difficult to reuse (no market for gypsum), and difficult to landfill.

Economics

The dry process is a relatively low-cost solution. Raw materials for these processes are cheap. Capital and operating costs are typically less than for wet scrubbing. Investment costs are around EUR 15 – 20 million, and operating costs are around EUR 2 – 3 million/yr (lime cost + landfill waste disposal).

Reference literature

[163, FWE 1999], [151, Sema, Sofres 1991], [200, Gilbert 2000], [221, Italy 2000].

4.5.6.4 Seawater scrubbing**Description**

Seawater scrubbing uses the natural alkalinity of the seawater to remove SO₂. More information can be found in Section 4.23.5.4.

Achieved environmental benefits

SO₂ recovery can be as high as 99 %. In order to reduce the particulate emissions to the seawater, a particulate abatement technique should be included before the flue-gas is treated in the seawater scrubber. Seawater scrubbing transfers sulphur emissions from air as SO₂ to the sea as SO₄, with a significant reduction in the overall environmental impact.

Cross-media effects

Particulates containing metals (e.g. V, Ni, Sb) and other pollutants from the flue-gas are transferred to the seawater. The sulphur content of the effluent seawater from the process itself is increased by only approximately 3 %. Seawater pumping and compression facilities increase the electricity consumption of the plant.

Operational data

The system needs electrical power (seawater pumps, aeration fans and flue-gas fans) and seawater. The seawater flow required for treating the 497 t/h mixed flue-gas stream received from a RCC unit (with CO boiler) and a SRU is 5 000 m³/h in the Statoil refinery of Mongstad (Norway). The seawater scrubber outlet temperature must be 25 °C. The seawater is further mixed with cooling water and the mixed temperature is around 15 °C.

In the Mongstad refinery, SO_x emissions from the RCC unit (310 kg/h) and the SRU tail gas (521 kg/h) were abated to 31 kg/h (>96 % reduction), as a yearly efficiency average in 2008.

It is feasible to use spent cooling water, for example, when seawater is used as cooling water. The need for seawater is around 30 m³/h for treating 1 000 Nm³/h of flue-gas with a SO_x concentration from 3 000 to 4 000 mg/Nm³. Special attention should be paid to minimise corrosion and the maintenance costs derived from it.

Applicability

The feasibility of applying seawater scrubbing depends on site-specific factors. The process requires access to large amounts of seawater at a competitive cost and high seawater circulation in the areas of the inlet and the outlet. It is fully applied for fuels with up to 1.5 % sulphur content. This system should be applied after a high particulate abatement removal technique to minimise as much as possible the contamination of the sea environment by particulates (containing metals).

Economics

Seawater scrubbers' annual costs depend on size and SO_x input/output. The cost is comparable to wet scrubbers. Typical investment costs are in the order of EUR 60/net kW output of the power plant. The main operating cost is the electrical power for operation of the technique.

Driving force for implementation

Reduction of SO₂ emissions.

Example plants

This system has been applied to some power plants around the world (e.g. Norway) and one proven commercial application for the RFCC flue-gas (after an ESP filtration) operated by Statoil in Mongstad (Norway).

Reference literature

[212, Power 2000]

4.5.7 FCCU abatement techniques' performance and emissions variability

Table 4.31 shows the achieved emissions values expressed as minimum and maximum monthly concentrations (at 3 % O₂ level) observed from continuous monitoring for a number of FCC units in Europe for dust, SO₂ and NO_x and the determining conditions of operation or the currently applied techniques at these units. [145, TWG CONCAWE 2012]

Examples of daily variability of dust, SO₂ and NO_x emissions to air are shown in Figure 4.25, Figure 4.26, Figure 4.27 and Figure 4.28.

According to a survey carried out in 2012 on 12 out of 14 sites currently operating in Italy, the trends of the emissions change from site to site and from plant to plant. According to information provided in this survey, emissions to air from FCCUs are depending on technical and construction features, mainly linked to a process configuration designed to crack heavy products, characterised by different qualities of feed and its origin (coming from other refinery units or imported to the site). Thus, a broad daily variability of the emissions of SO₂ and NO_x occurs. [278, TWG-IT 2012]

Table 4.31: Abatement techniques and reported performance data for a sample of European FCC units

| Refinery | Dust | | | SO ₂ | | | NO _x | | |
|----------|---|---|--|---|---|--|---|---|---|
| | Monthly min. mg/Nm ³ at 3 % O ₂ | Monthly max. mg/Nm ³ at 3 % O ₂ | Technique | Monthly min. mg/Nm ³ at 3 % O ₂ | Monthly max. mg/Nm ³ at 3 % O ₂ | Technique | Monthly min. mg/Nm ³ at 3 % O ₂ | Monthly max. mg/Nm ³ at 3 % O ₂ | Technique |
| J | 27 | 47 | Secondary Cyclones, 4-stage ESP and ammonia injection | | | | | | |
| E | 11 | 21 | TSS + 4-field ESP. Ammonia injected when needed; no continuous use. | | | | | | |
| G | 15 | 27 | TSS + 4-field ESP | 450 | 900 | HT (80 %) of feed + to give average S content of 0.3 % | 120 | 175 | HT (80 %), low-NO _x CO promotor. Effect of HT on NO _x unquantified |
| XY | 18 | 38 | 3-field ESP with ammonia injection | 600 | 650 | Complex feed with average 26 % HT residue | 80 | 395 | Complex feed with average 26 % HT residue |
| L | 26 | 40 | 3-field ESP with ammonia injection (30 mg/Nm ³ of NH ₃) | | | | | | |
| S | 38 | 55 | TSS + 3-field ESP. No ammonia injection | | | | | | |
| ZA | 65 | 81 | TSS | | | | | | |
| H | 62 | 85 | Sec. cyclones, regular (4-hourly) soot blowing. Spot sample gives 66 mg/Nm ³ of 85 for opacity meter. | | | | 650 | 830 | |
| U | 60 | 90 | Three-stage separators | 380 | 700 | Partial hydrotreatment of feed | 220 | 590 | DeNO _x Additive |
| V | 65 | 103 | TSS | 692 | 2485 | Partial hydrotreatment of feed | 176 | 522 | DeNO _x Additive. NO _x higher at 490 for month following start-up. |
| X | 110 | 130 | TSS | 350 | 750 | Feed is hydrotreated | 180 | 300 | Feed is hydrotreated |
| Z | 120 | 130 | TSS (limited data-set) | | | | | | |
| N | 60 | 155 | TSS | 750 | 1400 | Hydrofined feed | 280 | 700 | Antimony additive used to control adverse effects of Ni deposition on catalyst |
| YZ | | | TSS + ESP – 3-stage (no data) | 650 | 1200 | | 60 | 130 | Not known |
| 1 | | | | 410 | 590 | Low-S feed and Sulphur-Reducing Additive (before additive was 900) | | | |
| 2 | | | | 800 | 1200 | Feed S content below 1 % | | | |
| D | | | | 6 | 23 | Fully Hydrotreated Feed to 0.03 % S | 100 | 150 | Fully Hydrotreated Feed 0.03 % S. One month NO _x is at 40 mg/Nm ³ but this appears atypical |

Source: [145, TWG CONCAWE 2012]

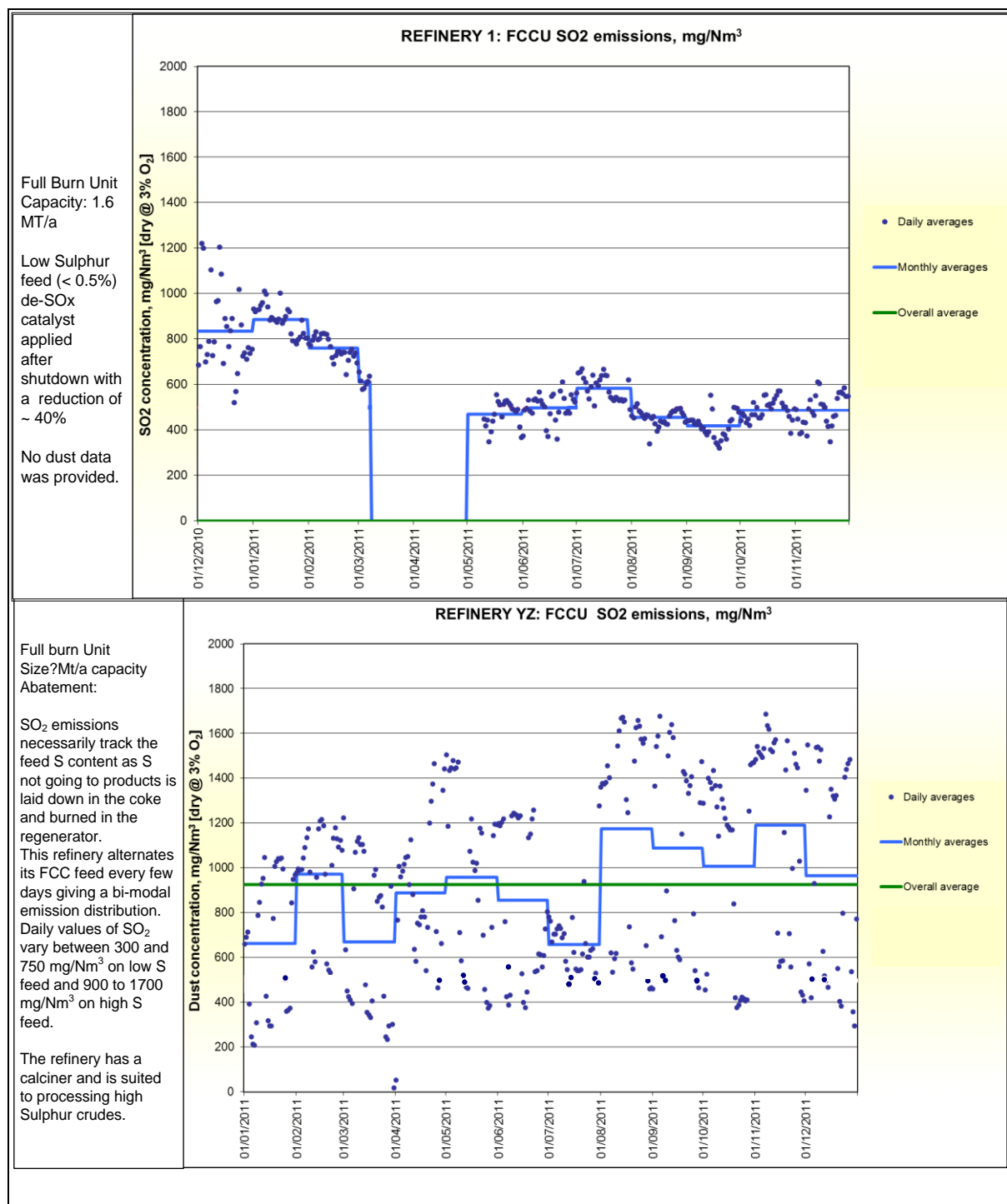


Figure 4.25: Daily variations of SO₂ emissions from FCC units: Example of sites 1 and YZ

The graphs presented in Figure 4.25 and Figure 4.26 illustrate some examples of the daily variations of SO₂ emissions reported for a number of European FCC units and the available contextual information.

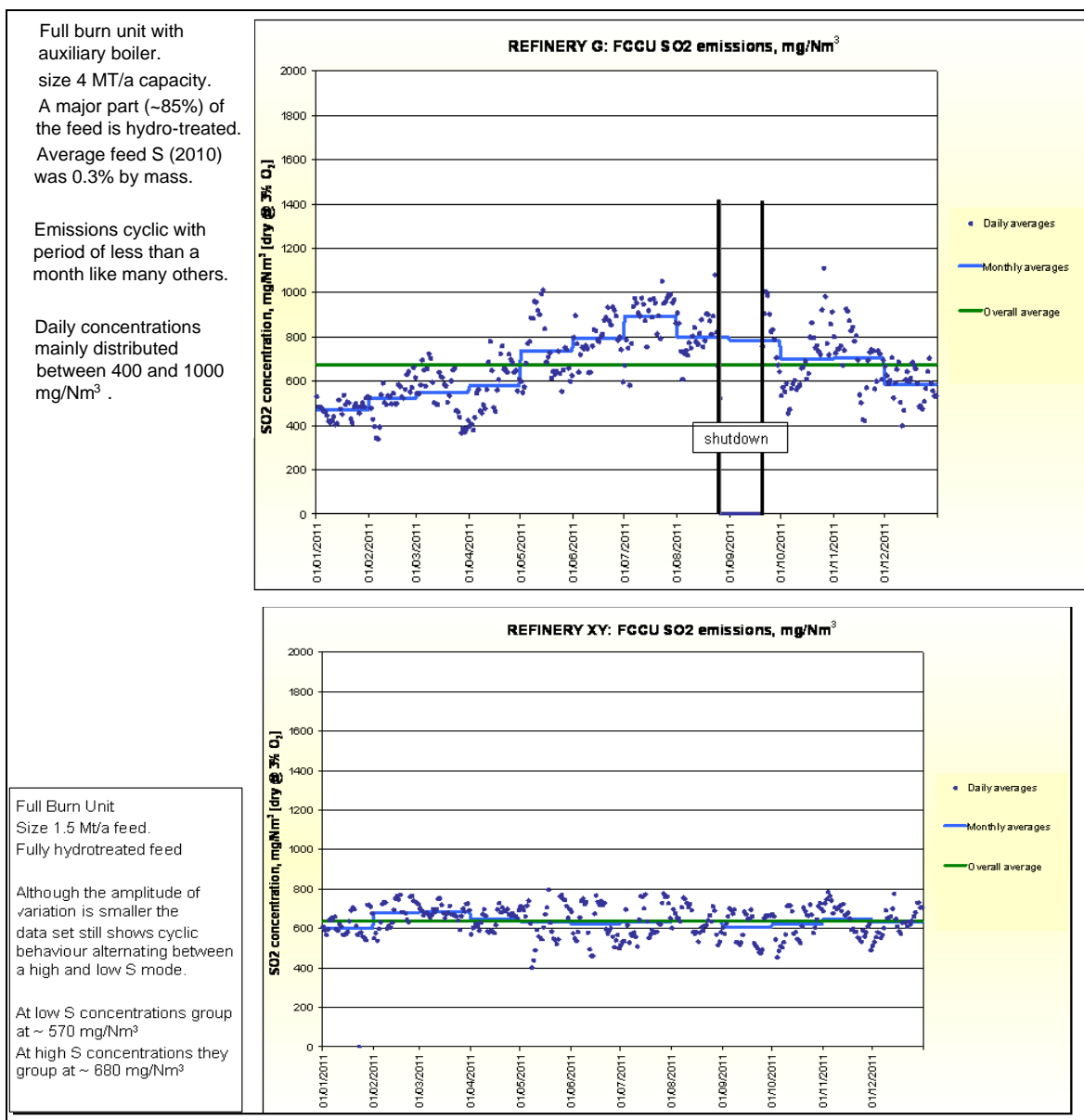


Figure 4.26: Daily variations of SO₂ emissions from FCC units: Example of sites G and XY

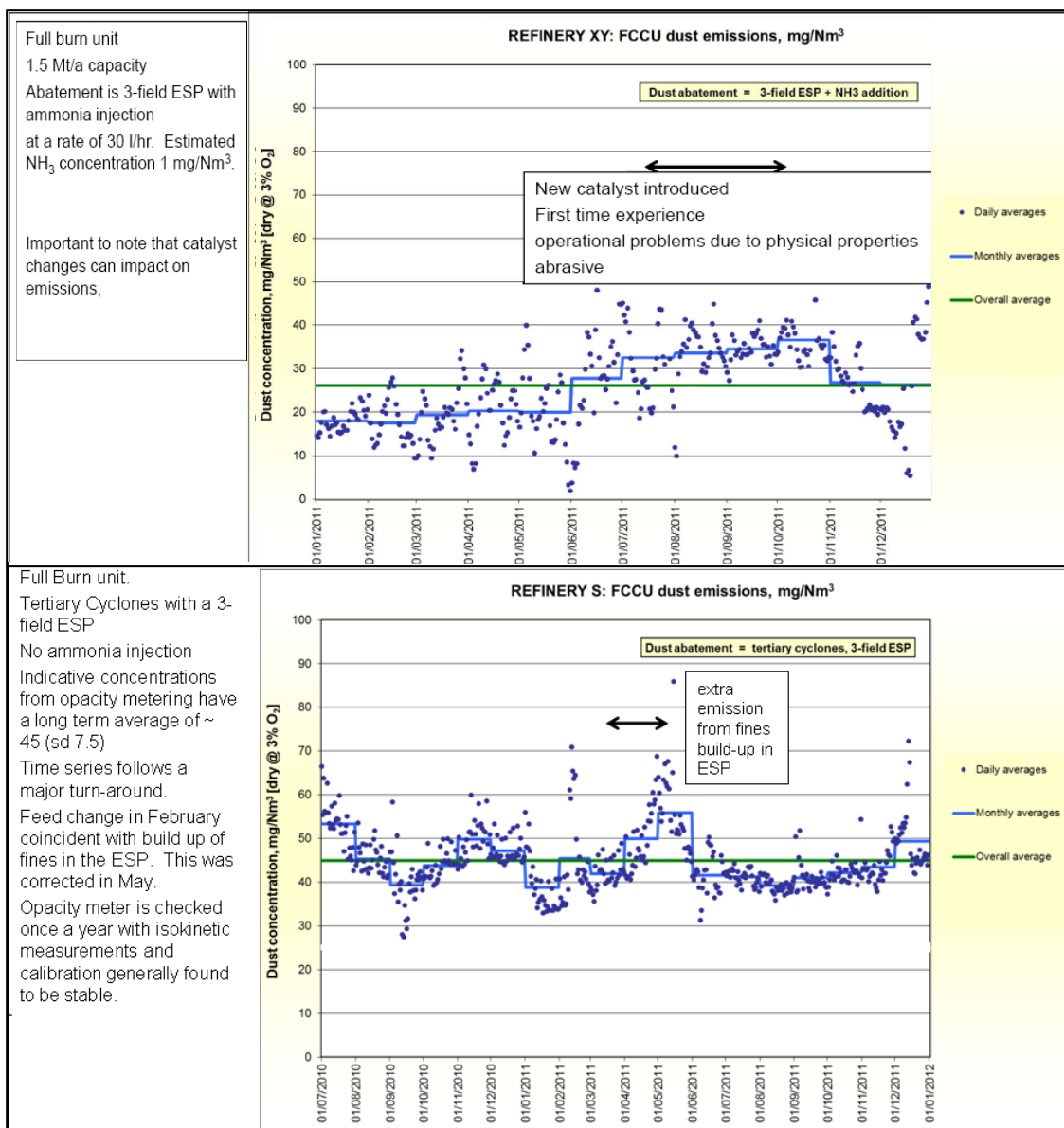


Figure 4.27: Daily variations of dust emissions from FCC units: Example of sites XY and S

The graphs presented in Figure 4.27 illustrate some examples of the daily variations of dust emissions reported from the continuous monitoring of two European FCC units.

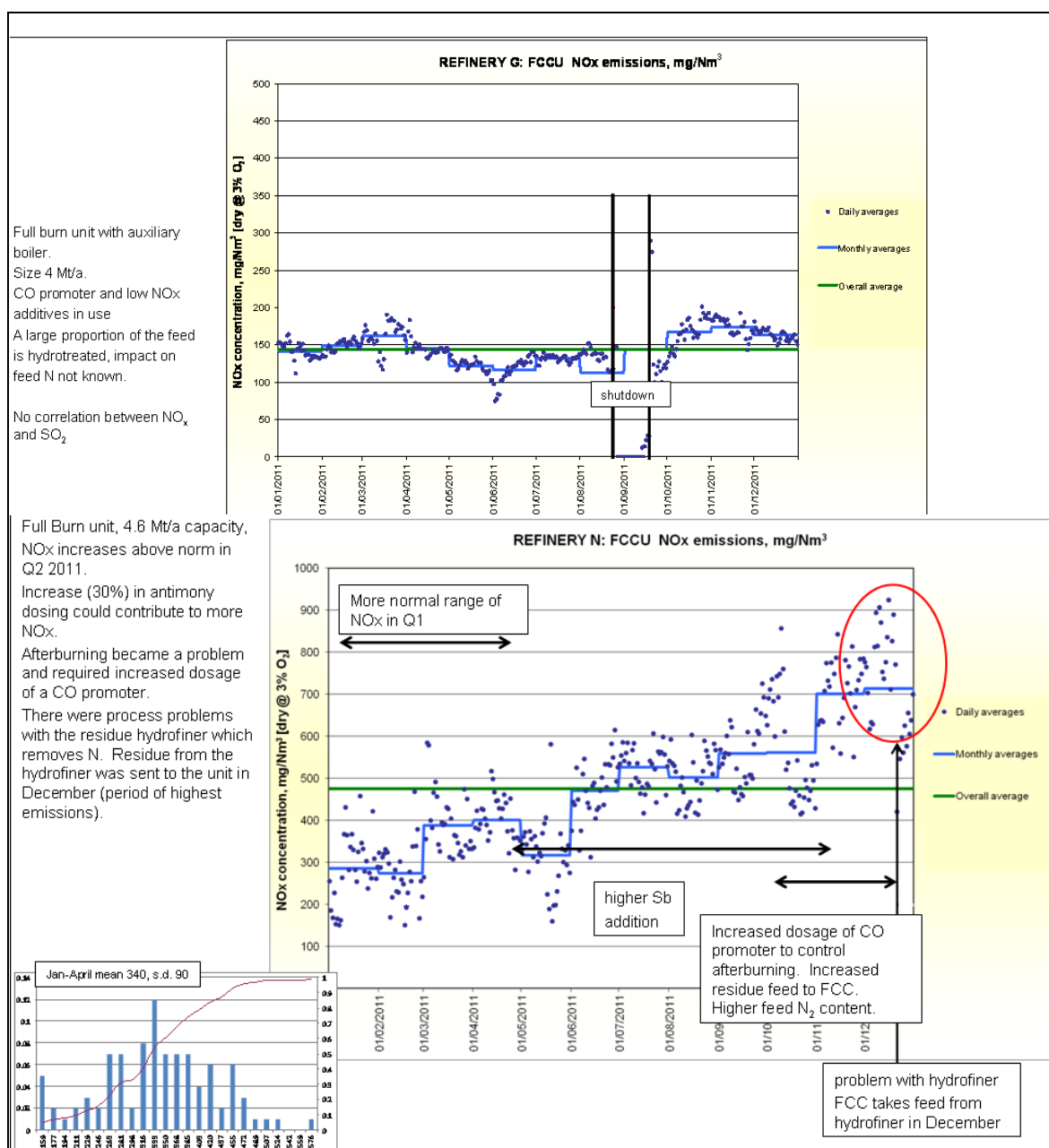


Figure 4.28: Daily variations of NO_x emissions from FCC units: Example of sites G and N

The graphs presented in Figure 4.28 illustrate some examples of the daily variations of NO_x emissions reported from the continuous monitoring of two European FCC units.

4.5.8 Waste management techniques

See previous sections for selection of catalyst, control of the emissions of particulates and proper management of product and slurry tank bottoms that can reduce the generation of waste.

4.6 Catalytic reforming

The first two techniques considered are process-integrated techniques and the rest are techniques for the prevention or control of emissions from the catalytic reforming processes.

4.6.1 Reduction and/or substitution of catalyst promoter (chlorine precursor)

Description

During the regeneration of the catalyst, organic chloride is needed for effective reforming catalyst performance: a chloride injection is needed to re-establish the proper chloride balance in the catalyst and to assure the correct dispersion of the metals. Ozone-depleting substances (e.g. carbon tetrachloride) were initially used during the regeneration. According to Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer, the placing on the market and use of such substances, particularly carbon tetrachloride, are now prohibited.

Achieved environmental benefits

Optimisation and reduction of the use of catalyst promoters. Use of substitutes for ozone-depleting substances, such as perchloroethylene.

Cross-media effects

Due to the use of chlorinated compounds, the possibility of emissions of dioxins and furans during regeneration has been detected.

Operational data

Promoters should be handled in enclosed systems.

Example plants

Most refiners have switched to less ozone-depleting substances, such as perchloroethylene, during the regeneration of the reforming catalyst.

Reference literature

[156, MCG 1991].

4.6.2 Cleaning of the regeneration flue-gas

Description

The regeneration vent gas can contain traces of HCl, Cl₂, CO, SO₂, hydrocarbons, dioxins and furans. The storage and handling of organic chlorides used during the regeneration may also lead to releases. In some designs, the regeneration vent gas may be routed over an adsorption bed, through a scrubber, or combined with a basic water wash system.

Achieved environmental benefits

Adsorption beds, water or caustic scrubbers, and basic water wash systems lead to a reduction in the emissions of trace components in the regeneration vent gas and removal of the majority of the dioxins and furans from air emissions. However, due to the hydrophobic characteristic of dioxins and furans, a part may pass through such cleaning systems.

Cross-media effects

When the design includes a scrubber, the recirculated and bleed streams from the regeneration flue-gas wash should be sent to the waste water treatment plant. Due to the low pH of this waste water stream, neutralisation prior to biological treatment may be necessary. The use of scrubbers can move some dioxins from air to water emissions.

Applicability

Fully applicable to new units and with general provisions about retrofitting existing units, taking into account the current design (impact on pressure and temperature balances, existing structures, plot space availability, etc.)

Economics

No data available for this particular application.

Driving force for implementation

Reduction of air pollutants.

Reference literature

[163, FWE 1999], [207, TWG 2001].

4.6.3 Electrostatic precipitator in the regeneration flue-gas

Description

Regenerator flue-gas containing HCl, H₂S, small quantities of catalyst fines, and traces of Cl₂, SO₂ and dioxins can be sent to an electrostatic precipitator prior to release to the atmosphere. Emissions generated by other activities, such as venting during catalyst regeneration or replacement and plant cleaning, may be sent to the ESP.

Achieved environmental benefits

Reduction of particulate content in the flue-gas coming from the regenerator.

Cross-media effects

See Section 4.23.4.2.

Operational data

None available for this particular application. For general data, see Section 4.23.4.2.

Applicability

Emissions from continuous regeneration sections require particular attention. No example of an ESP used for continuous catalyst regeneration has been reported.

Economics

None available for this particular application. For general data, see Section 4.23.4.2.

Driving force for implementation

Reduction of particulate emissions during the catalyst regeneration.

Reference literature

[163, FWE 1999], [207, TWG 2001]

4.6.4 Reduction of PCDD/F emissions from catalytic reforming

Description

Referring to Section 3.6 and the sections in 4.6 on catalytic reforming, dioxins are typically formed in the three types (continuous, cyclic and semi-regenerative) of catalytic reforming during the regeneration of the catalyst.

De novo reaction is the chemical reaction that produces dioxins and furans. This reaction is favoured between 200 °C and 450 °C and in the presence of iron oxide particles produced from corrosion which act as a catalyst.

If the regenerator flue-gas is treated in a water scrubber (e.g. Section 4.6.4) the dioxins appear detectable in waste water from the scrubber, but they are not detected after the WWTP, possibly due to dilution effects.

In some other cases, because of the use of other techniques such as fixed bed filters, there is a combined reduction of chlorine and dioxins. In some cases, activated carbon has been used to remove dioxins. Another technique that has been used includes the recirculation of vent gases; however, it is not clear how it can reduce the emission of dioxins.

The study of dioxins emissions from reformers and how the regeneration conditions may affect these emissions can be a good way to start to understand and solve the problem.

Achieved environmental benefits

Knowledge of origin and control of the dioxins emissions.

Cross-media effects

Some dioxins from the regenerator gases may be transferred to water via scrubbing.

Operational data

Preem refinery Lysekil (SE) installed a continuous regeneration gas recycling loop in 2001. The waste gas from the regeneration is recycled to the catalyst where chlorides, chlorinated hydrocarbons and dioxins are re-adsorbed. Emission of dioxins from the reformer was 0.323 g TCDD-eq/yr before installation. Emission after the abatement technique installation was 0.004 5 g TCDD-eq/yr (average). The following reductions for dioxins and other parameters were achieved:

- dioxins: 99 %;
- chlorobenzene: 94 %;
- PCB: 93 %;
- chlorides: 83 %.

A similar technique is applied with a discontinuous regeneration at Preem refinery Gothenburg. In that case, the gases are treated in a scrubber and after that the water is filtered through active carbon.

Applicability

No data received.

Economics

No data received.

Driving force for implementation

Knowledge of the formation of dioxins in the regeneration of the catalysts.

Example plants

Some EU refineries have already applied and monitored dioxin emissions from catalytic reformers. Techniques such as chlorine traps and the recirculation of vents have not been reported to be applied to semi-regenerative reformers due to the use of basic water wash systems in these designs. Efficient abatement techniques are used at two Swedish refineries (see Operational data paragraph).

Reference literature

[77, REF TWG 2010], [207, TWG 2001], [268, CieGötaverken Miljö Cie 2012], [269, Axens IFP 2012]

4.7 Coking processes

The first four techniques considered in this section are coking processes. The information given is intended to help assess how well coking processes can perform from the environmental point of view. The rest of the techniques are related to the cleaning of the coke gas, the use of the coking process to destroy solid residues/sludges and, finally, those techniques related to the abatement of pollution generated by the coking processes.

4.7.1 Techniques to prevent emissions from delayed coking

Description

A description of this process can be found in Section 2.7. Following is a list of the techniques that may be applied to the delayed coker to prevent emissions.

- Preventing incondensable vapours generated in the coking processes from passing to the flare system by sending them to a gas separator unit for passing to the refinery FG network.
- Passing pressure reliefs from the coke drums to a closed blowdown system, e.g. the quench tower.
- Techniques for coke drum pollution control including carrying the final venting to gas flare gas compressor to recover as refinery fuel gas, rather than flaring, and sending condensed water to the WWTP.
- Using water in the delayed coker as described in Section 4.7.6.
- Using the steam generated in this process to heat up other refinery processes.
- Improving heat integration: the delayed coking process itself has a low level of heat integration. The heat to maintain the coke drums at the coking temperature is supplied by heating the feed and the recycle stream in a furnace. However, the atmospheric residue and/or vacuum residue can be fed straight into the delayed coking unit without intermediate cooling, which results in a high heat-integration level between the different units and saves a considerable amount of capital on heat exchangers.
- Using coking gas. The energy efficiency of the coker can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined cycle units appears in Section 4.10.

Achieved environmental benefits

Reductions of VOC emissions, recovery of products and a reduction of H₂S emissions are achieved when applying some of the above-mentioned techniques. Water reuse is also promoted by the application of these techniques.

Cross-media effects

No data received.

Operational data

Some operational data of delayed cokers can be found in Section 3.7.

Applicability

No data available.

Economics

The typical investment of a full delayed coker (based on 1 Mt/yr straight run vacuum residue feed, US Gulf Coast, fuel-grade coke, including vapour recovery) was estimated at USD 136 250 – 218 000 per t/yr in 1998.

Driving force for implementation

Production process.

Example plants

Many delayed processes exist in Europe, even though coking processes in general are more commonly used in the US. In 2011, 67 delayed coking units were installed worldwide.

Reference literature

[76, Hydrocarbon processing 2011], [148, Irish EPA 1993], [163, FWE 1999], [168, VROM 1999].

4.7.2 Techniques to prevent emissions from fluid coking**Description**

A description of this process can be found in Section 2.7. General abatement techniques, such as ESPs, (see Section 4.23) are applicable to fluid coking units. Another technique that can be used to prevent emissions or increase energy integration in fluid coking is to use the coking gas in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined cycle units appears in Section 4.10.

Achieved environmental benefits

Emission factors for fluid coking (units in kg/1 000 litres of fresh feed) are given in Table 4.32.

Table 4.32: Emission factors for fluid coking

| Process | PM | SO _x (as SO ₂) | CO | HC | NO _x (as NO ₂) | Aldehydes | NH ₃ |
|---|--------|--|-----|-----|--|-----------|-----------------|
| Fluid coking units <i>uncontrolled</i> | 1.5 | NA | NA | NA | NA | NA | NA |
| Fluid coking with <i>ESP and CO boiler</i> | 0.0196 | NA | Neg | Neg | NA | Neg | Neg |
| Neg: negligible NA: not available | | | | | | | |

Cross-media effects

No data.

Operational data

This system operates under fluidised bed conditions.

Applicability

No data.

Economics

Investment (US Gulf Coast 1996): USD 10 000 – 13 200 per m³/d.

Driving force for implementation

Production process.

Example plants

A number of fluid coking units exist around the world.

Reference literature

[172, MRI 1997].

4.7.3 Techniques to prevent emissions from the calcination process

Description

A brief description of this process can be found in Section 2.7. Certain techniques can be applied to the calcination process to prevent emissions, and some of those considered to be beneficial are included in the following list.

- The kilns can be directly fuelled by coke gas or coke fines, driving off volatile matter and burning it within the kiln.
- The hot stream of waste gas from the calcination of petroleum coke in rotary kilns contains considerable quantities of particulate matter, which, possibly after heat recovery from the waste gas, is separated with suitable filter devices, e.g. high-efficiency multi-cyclones, bag filters and electrostatic precipitators (see also Section 4.7.7). During calcination in multiple-hearth furnaces, particulate abatement techniques are not usually used because of the comparatively low emissions in the waste gases.
- The unburnt gases from the calciner are burnt in an incinerator, then passed through a waste heat boiler before being released to the atmosphere via a dust collection system.
- The SCR technique (as described in Section 4.10.4.6) and the SNCR technique (as described in Section 4.10.4.7) may be applicable to these calcination off-gases for efficient NO_x reduction.
- The calcined coke discharges to the rotary cooler where it is cooled by direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and a wet scrubber.
- Collected fines from the dust abatement techniques should be conveyed to a silo with exhaust air filters. Collected cyclone fines may be recycled to product, used within the refinery, or may be sold as product.

Achieved environmental benefits

Some of the techniques mentioned above increase the heat integration of the calciner, reducing the consumption of fuel in the refinery. Others decrease the amount of particulates emitted to the atmosphere, reusing the coke fines generated during the calcination process. The emission values for petroleum coke production plants attainable in continuous operation are presented in

Table 4.33. These values can be achieved by applying the techniques mentioned above.

Table 4.33: Emission values for petroleum coke production (calcination of green coke)

| Emission component | Values attainable in continuous operation (Emission values as half-hourly mean values in mg/Nm ³ at 3 % O ₂ unless stated otherwise) |
|--|--|
| Particulate (dust) emissions | 20 – 60 (at boiler stack - daily - no O ₂ correction) 40 – 150 (at cooler or combined boiler/cooler stack - daily - no O ₂ correction) |
| Particulate (dust) components: Ni, V and their components (given as Ni and V total) | 3 - 15 |
| NO _x (as NO ₂) | 450 – 875 (no NO _x abatement technique included) |
| SO _x (as SO ₂) | (no SO ₂ abatement technique included) 1 100 – 2 300 ⁽¹⁾ 300 – 700 ⁽²⁾ |
| CO | 100 |
| HC (given as total carbon) | 20 |
| ⁽¹⁾ As a daily average. | |
| ⁽²⁾ As a daily average for low-sulphur coke. | |

Taking into account the energy-saving additional devices and relevant temperature window availability, a further significant reduction of NO_x may be achieved using SCR or SNCR.

No examples of the use of SCR techniques have currently been reported in calciner service in the EU.

Operational data

Some operational data of petroleum coke calciners can be found in Sections 2.7 and 3.7.

Flue-gas flow rates from the calciner (3 % O₂ dry gas) are typically between 1.8 Nm³ and 3 Nm³ per tonne of coke feed (wet feed rate into the calciner). Variation can be connected to the type of coke, and the type of flue-gas (e.g. possible combination of cooler and boiler stacks).

Additional data of emissions to air of NO_x, SO_x, and dust at the calciner stack from some European sites (reported monitoring) are provided together with the associated information on techniques and operating conditions in Table 4.34.

Table 4.34: Emissions to air from a sample of calciners operated at European refineries

| Refinery calciner stack code | Type of calciner | Type of green coke | Techniques in place | SO ₂ | | NO _x | | Dust | |
|------------------------------|----------------------|--|---------------------|----------------------|----------------------|--------------------|--------------------|-------------------|--------------------|
| | | | | Min. monthly | Max. monthly | Min. monthly | Max. monthly | Min. monthly | Max. monthly |
| SA1 Shared by 2 calciners | Rotary kiln | Two different grades: anode and graphite | Cyclones | 600 | 1 200 | 500 | 750 | 28 ⁽¹⁾ | 62 ⁽¹⁾ |
| SB1 | Rotary kiln | Single grade | Cyclones | 1 500 | 2 200 | 280 | 380 | 55 ⁽¹⁾ | 152 ⁽¹⁾ |
| G | Rotary hearth (disk) | Sulphur content: 1.6 % | Cyclones + ESP | 2 100 | 2 500 | 280 | 380 | | <20 |
| K | Rotary kiln | NA | Cyclones + ESP | 2 000 ⁽²⁾ | 2 300 ⁽²⁾ | 370 ⁽²⁾ | 430 ⁽²⁾ | | <10 |

All concentration values expressed as mg/Nm³ at 3 % O₂ content.
⁽¹⁾ For S refinery, dust emissions converted from actual 8 % O₂ content provided data.
⁽²⁾ For K refinery, all values converted from actual 7 % O₂ content provided data.
Source: CONCAWE 2012

Figure 4.29 shows the variability of emissions to air, over a long time span, of SO₂, NO_x and dust from two calciners connected to a unique stack (named SA1 in Table 4.34) and operating on two grades of coke (with different sulphur contents). The SO₂ and NO_x emissions appear to be mainly influenced by the type of coke, whereas the dust emissions are less influenced (abatement technique in place for dust only).

For secondary NO_x abatement techniques, it is reported that one site operating a calciner equipped with SNCR reports a daily value of less than 350 mg/Nm³. [146, TWG DE 2012]

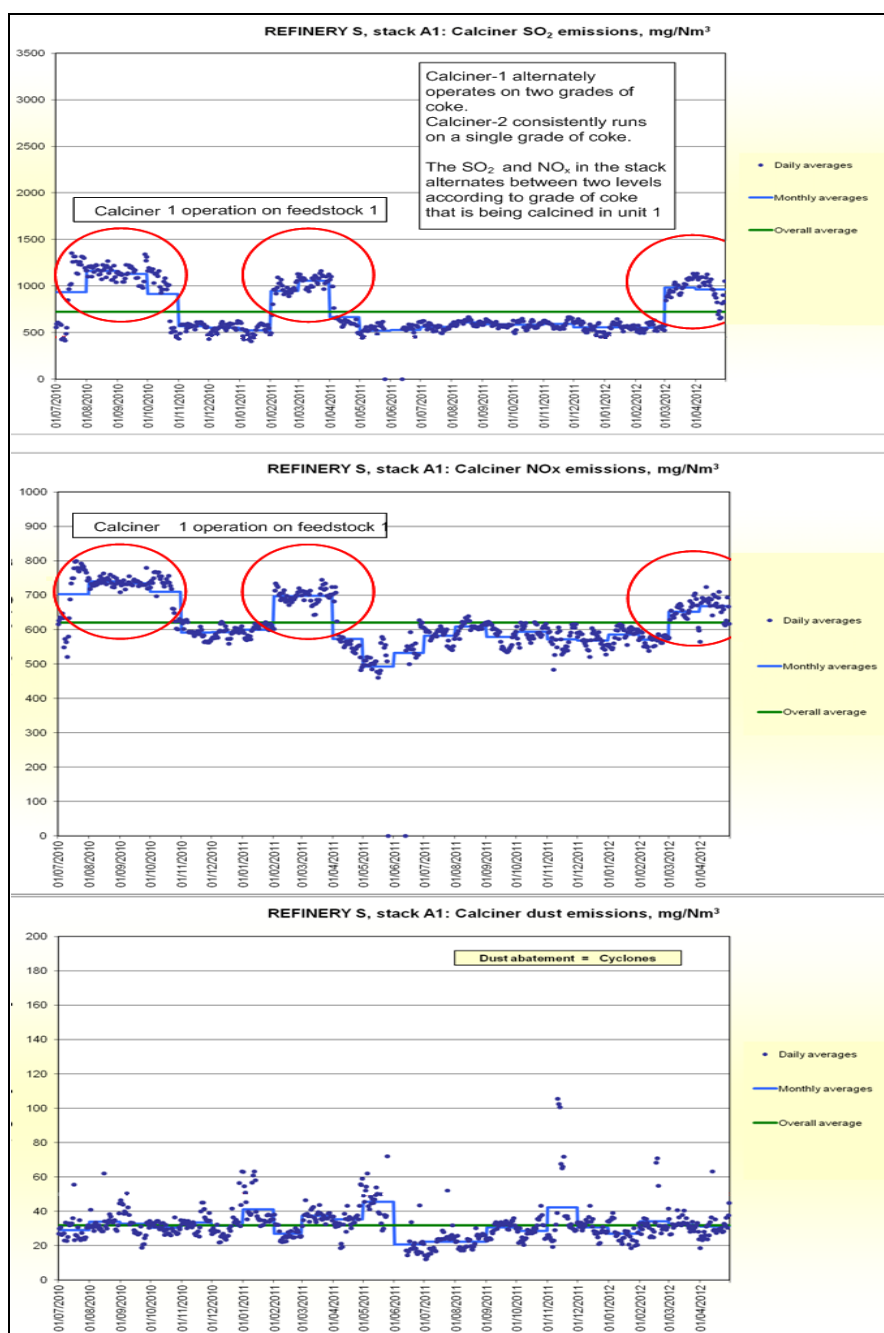


Figure 4.29: Variability of emissions to air: Example of two calciners (rotary kilns) with a common stack

Applicability

Applied to coke produced by delayed cokers and fluid cokers.

The applicability of the techniques for dust abatement is linked to the type of calciner in use: rotary kiln or rotary hearth (disk). Table 4.34 shows that multistage cyclones are commonly used and that an ESP may be installed at both rotary kiln or rotary hearth calcining processes.

No examples of abatement techniques for SO_x abatement at the calciner have been reported in the EU.

No primary techniques have been reported to be applicable for NO_x abatement at the calciner.

For secondary NO_x abatement techniques, one site equipped with SNCR reports a daily value of <350 mg/Nm³. [146, TWG DE 2012]

Economics

A very brief preliminary evaluation for the retrofitting of SCR on two calcination kilns gives the following costs that should be taken only as first estimations of the order of magnitude:

- Design N°1: capital costs EUR 24.24 million, operating costs EUR 0.920 million per year (2007); estimated quantity of NO_x abated 601 t/yr (EUR 7 450/t for 15-year lifetime, 12 % rate assumed) for an 85 % reduction yield;
- Design N°2: capital costs EUR 20.8 million, operating costs EUR 0.71 million per year (2007); estimated quantity of NO_x abated 563 t/yr (EUR 6 672/t for a 15-year lifetime, 12 % rate assumed) for an 85 % reduction yield.

Driving force for implementation

Production process. For certain applications, green coke produced by the delayed coker should be calcined before being used or sold.

Example plants

Many examples exist in Europe and around the world. Multiple-hearth furnaces have been extensively applied to waste incineration. The majority of facilities that calcine coke utilise a rotary kiln. The last two calcining facilities built were rotary kilns.

Reference literature

[90, COM 2011], [167, VDI 2000], [174, HMIP UK 1995], [207, TWG 2001], [245, M. H. F. Services 2001], [Site questionnaire n°42].

4.7.4 Flexicoking

Description

A brief description of this production process can be found in Section 2.7. Some techniques that may be applied to prevent emissions from the flexicoker are the following.

- The flexicoking process has a high level of heat integration. The only source of heat in the flexicoker process is the gasifier, where the coke is partially oxidised. The remainder of the heat in the coker gas is recovered by generating steam. The energy efficiency can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. See Section 4.10.
- As coke cutting from drums is not needed, emissions and dirty effluent generation are avoided, as opposed to delayed coking. Moreover, the sulphur components from the coke gas are easy to eliminate. Some 84 – 88 % w/w of the hydrocarbon feed is recovered as hydrocarbon product, the remainder is converted into CO, CO₂ and H₂O.
- The coke gas from the heater is passed through a cyclone set to remove the coarser coke particles and is subsequently cooled by the generation of high-pressure steam and by preheating the boiler feed water. About 75 % of the coke fines which pass through the two stages of heater cyclones are recovered in tertiary cyclones. Almost all the coke fines which escape the tertiary cyclones are scrubbed out in the Venturi scrubber. The water slurry from the Venturi scrubber is steam-stripped to remove absorbed hydrogen sulphide and ammonia.

Achieved environmental benefits

The environmental benefits from the described techniques include:

- an increase in the energy efficiency of the flexicoking process;
- less waste generated than delayed coking;
- prevention of particulate, hydrogen sulphide and ammonia emissions.

Cross-media effects

No data received.

Operational data

Some operational data for flexicokers can be found in Sections 2.7. and 3.7.

Applicability

Fully applicable. However, because the products from flexicoking are different to those from other coking processes (e.g. no coke is produced), refinery product requirements should be considered when implementing this option.

Economics

Typical investment (based on US Gulf Coast 1996): USD 15 100 – 19 500 per m³/d.

Driving force for implementation

The implementation is mainly driven by the site production strategy.

Example plants

Many examples exist in Europe (the Netherlands, Greece), the US (Texas, California) and the rest of the world (Japan, Venezuela).

Reference literature

[183, HP 1998], [209, Pozo 2000].

4.7.5 Use of oily sludges and/or waste as coker feedstock

Description

In refineries with a coker, oily sludges, sludges from the waste water treatment, and waste can be destroyed in the coker (delayed, fluid or flexicoker). If coke is produced, the coke quality produced should remain acceptable (with respect to further use as fuel within/outside the refinery or as material for other purposes). Many oily sludges can be sent to a coking unit where they become part of the refinery products.

Achieved environmental benefits

Reduction of the amount of sludge and/or waste produced in the refinery. A refinery with a coker is able to greatly reduce its oily sludge production. High-quality coke requirements can, nevertheless, restrict its use.

Cross-media effects

Typically there is a reduction in the quality of the coke produced.

If sludges from the waste water treatment are included as feedstock to the coker, part of the water needs to be eliminated (e.g. by vacuum evaporation or in the blowdown system) if the amount of residues is to be maximised.

Applicability

A balance must be achieved between the amount of sludge waste sent to the coker and coke quality specifications. Coking operations can be upgraded, however, to increase the amount of sludge that they can handle.

The quantity of solids injected depends on the solids content of the slurry, typically being 2 – 10 %. Loading rates exceeding 40 kg of oil-free dry solids per tonne of coke are considered typical.

Generally, cokers are an attractive process-integrated reprocessing outlet for oily sludges, provided the sludge-on-feed ratio is kept below 1 – 2 %, depending on the required coke quality and the operability.

Economics

No information available.

Driving force for implementation

Reduction of waste generation in the refinery.

Example plants

The use of sludge as a feedstock is, at the time of writing (2010), commonly carried out by refineries where no high-quality coke is produced.

Reference literature

[174, HMIP UK 1995].

4.7.6 Water use in the cooling/cutting process

Description

Water used in the cutting/cooling operations is continuously recirculated with a bleed-off to the refinery waste water treatment. Settling and filtering over a vacuum filter enables the reuse of this water, resulting in a ‘closed-water loop’. For water make-up to the quenching and for cutting the water loop, various effluent streams can be used. For this task, treated effluent could be used. Collected water from any condenser, and from the draining of wet green coke, should be reused for coke drum quenching or drilling. This type of cooling is not used in any other process in the refinery, because of environmental concerns. More information about direct cooling (quenching) is found in Section 2.8.

Achieved environmental benefits

Reduced consumption of water in the refinery.

Cross-media effects

Cutting and cooling processes result in vapour emissions (partially recycled in the main fractionator), significant energy losses, substantial water use and severe water pollution. Bleeding of cutting water to the desalter has the potential to add solids to the effluent, so it is best to keep coker waters separate.

Operational data

The amount of make-up water required depends on the evaporation losses, loss with the coke product, and the bleed to other processes or to the waste water treatment plant, and is about 10 – 20 m³/h for a 10⁶ t/yr delayed coker unit.

Applicability

Applicable when delayed coking is used. Reuse of water is subject to restrictions of coke quality.

Driving force for implementation

Water reuse is typical in the delayed coking process and should be optimised as part of the site water management system.

Example plants

Many examples of this application exist worldwide.

Reference literature

[207, TWG 2001].

4.7.7 Handling and storage of the coke

Description

Several techniques are suitable to reduce particulate emissions that may occur during the handling of coke (green and calcined).

- Provided the green coke is kept wet, the handling between the discharge and the calciner feed hopper is not problematic. There is the possibility that parts of the receiving pit may dry out, although this is limited, as the coke is usually very wet and is covered with residual hydrocarbons which tend to make it stick together. The construction of wind-breaks around the pit might be considered. Careful design is essential, as bad design could make the situation worse. Complete enclosure of the pit and associated handling facilities is another possibility. The pits are very large and such an enclosure would be very expensive. A monitoring programme should be carried out to evaluate if this option is in fact necessary or desirable.
- Cutting the coke into a double-roll crusher and conveying it to an intermediate storage silo is another technique. The railway wagons are then loaded from the storage silo. This approach would collect, filter, and dewater the coke prior to storage.
- Another option is spraying the calcined coke with a very fine layer of oil, which sticks the dust fines to the coke. The use of oil is limited by its acceptability in further processing. The oil option has the added advantage of reducing unloading problems.
- Covering and depressuring conveyor belts.
- Using aspiration systems to extract or collect dust.
- Using an enclosed, hot blowdown system.
- Enclosing loading areas and maintaining positive/negative pressures, exhausting through bag filters. As an alternative, dust extraction systems can be incorporated with loading equipment.
- Conveying pneumatically collected fines from the cyclones to a silo with exhaust air filters. Dust collection systems are provided for handling, storage and loading, using bag filters. Collected fines are recycled to storage by enclosed means.

Achieved environmental benefits

Eliminates particulate matter releases (containing metals) to air of from this part of the process during routine operation, as well as from the storage of the coke.

Operational data

The storage silo provides a buffering capacity for process fluctuations and enables the controlled loading of railway wagons.

Applicability

Oiling coke (see bullet 3 described above) is sometimes practised in fluid and calcined coke, but is rarely applied with delayed coke.

Collecting and recycling coke fines (see Item 8 described above) is mostly applicable to calciners, fluid cokers and flexicoking units.

Economics

Investment costs of about EUR 30 million for a typical coking unit with a capacity of 1.5 Mt/yr may be expected for the storage system.

Driving force for implementation

Reduction of coke spillage. If the petroleum coke is cut directly from the coking units into railway hopper wagons, it may cause overfilling of the wagons, degrading the quality of the

spilled coke, and increase the amount of solids entering the waste water treatment system. Reduction of particulate emissions from the storage system of the coker is another driving force.

Example plants

Many examples are available in European refineries.

Reference literature

[156, MCG 1991], [167, VDI 2000], [204, Canales 2000], [207, TWG 2001].

4.7.8 Techniques to reduce air emissions

This section mentions where the abatement techniques may be used and describes the techniques used for the abatement of air pollutants.

4.7.8.1 Particulate abatement in coking processes

Description

Flue-gases and coke gas from coking processes normally contain coke particulates (including metals). Dust collection systems are used in all appropriate sections of the coking processes, in order to ensure the cleaning of:

- coke gas;
- gas produced during the coke cooling in the calciner;
- incinerated exhaust gases from the calciner which also contain coke fines. Hot flue-gases pass through a waste heat boiler equipped with a dust collection system.

In addition to the particulate abatement technique used in the FCC (cyclones or ESP in Section 4.5.5), bag filters can also be used for coking processes.

Achieved environmental benefits

Achievable release levels of particulate matter (values based on averaged continuous monitoring) from calciners and coolers are generally reported in the range of 20 – 150 mg/Nm³ (see Table 4.33). Best-performing plants (e.g. OMV in Burghausen, DE) achieve 10 – 20 mg/Nm³ with electrostatic precipitators (ESP) [28, Tebert et al.2009].

Cross-media effects

See Sections 4.5.5 and 4.23.4.

Operational data

See Sections 4.5.5 and 4.23.4. The application of an ESP for the control of particulate emissions from petroleum coke calciners has some difficulties in achieving the lower end of the range. The main reason is that coke is a very good conductor of electricity and consequently its surface is very difficult to electrically charge, and consequently difficult for the ESP to capture.

Applicability

See Sections 4.5.5 and 4.23.4. High-efficiency cyclones are easier to apply than ESPs.

Economics

Bag filters can be used at a cost of about EUR 5 million. Calciner boiler cyclones cost EUR 225 000 (1999). The economics for other types of systems are not available. An economic study done in a EU refinery in 1992 showed that the cost for an ESP for a calciner was high.

Driving force for implementation

To reduce the particulate emissions from the calciner.

Example plants

Many examples are available in European refineries: e.g. four cokers are installed in Germany, and four coking units in Spain.

Reference literature

[174, HMIP UK 1995], [249, Balik et al.1991], [221, Italy 2000], [210, Shawcross 2000], [167, VDI 2000], [207, TWG 2001], [28, Tebert et al.2009], [77, REF TWG 2010].

4.7.8.2 SO₂ abatement techniques**Description**

Sulphur oxides are emitted during the coking processes, especially during the calcination processes. The principal option to reduce sulphur dioxide releases from the process is the use of the lowest possible sulphur-content feedstocks. In practice, low-sulphur feeds are typically used for product quality reasons, since a substantial part of the sulphur remains fixed in the product. However, this option is not always possible and emissions of SO₂ may be significant, especially during the calcining process. To control these sulphur oxide emissions, the same abatement techniques that may be used in the FCC may also be used in this process (see Sections 4.5.6 and 4.23.5.4), with the exception of the DeSO_x catalyst additive.

Achieved environmental benefits

SO₂ concentrations of 25 – 300 mg/Nm³ are achieved when the techniques mentioned in Sections 4.5.6 and 4.23.5.4 are used.

Cross-media effects

See Sections 4.5.6 and 4.23.5.4.

Operational data

No data from sites using calciner SO₂ abatement techniques have been reported. For other applications, see Sections 4.5.6 and 4.23.5.4.

Applicability

Normally applied to calciner flue-gases.

Economics

See Sections 4.5.6 and 4.23.5.4.

Driving force for implementation

Reduction of SO₂ emissions.

Example plants

No examples of the use of these techniques and their associated emissions have been reported to the TWG.

Reference literature

[221, Italy 2000] and references in Section 4.10.6.

4.7.8.3 NO_x abatement techniques

Description

As already stated in Section 4.7.3, the SCR technique (as described in Section 4.10.4.6) and SNCR technique (as described in Section 4.10.4.7) may be applicable to calcination off-gases for an efficient NO_x reduction. Nevertheless, very limited example data have been made available on this topic.

Operational data

No detailed monitoring data from sites using NO_x abatement techniques at the calciner have been reported.

Applicability and example plants

The use of the SCR technique was not reported at calciners in the EU. One German refinery site reports the use of SNCR for two calciners.

4.7.8.4 Cleaning of the coking gas

Description

After the coking gas has been cleaned to remove particulates and to recuperate part of its heat, it is heated and passed over a catalyst bed in the COS converter, where COS is converted to H₂S. The gas is then cooled and most of the water is condensed. The H₂S is recovered from the coke gas in an amine treater for ultimate recovery of sulphur (see amine treating of refinery fuel gas in Section 4.23.5.1). Clean low-sulphur coking gas can either be used as a site fuel or can be sold as low calorific-value gas. Figure 4.30 shows a scheme of that process.

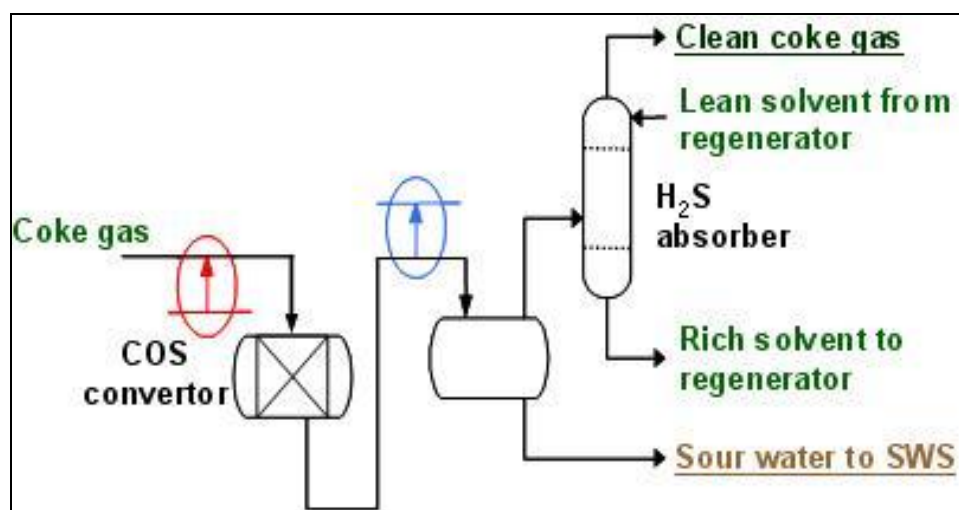


Figure 4.30: Coking gas treatment

Achieved environmental benefits

Reduction of emissions of H₂S (in the range displayed in Table 4.80) and COS.

Cross-media effects

Increased use of the amine scrubbing system and increased energy consumption of the COS converter.

Operational data

For amine scrubbing, see Section 4.23.5.1.

Applicability

Amine scrubbing is applied to all types of cokers. COS converters are applied to some units.

Economics

The economics data of the amine absorption of H₂S can be found in Section 4.23.5.1.

For existing coking units, the applicability of the retrofit is reported to be limited due to the high investment and operational costs.

Driving force for implementation

Cleaning of the coke gas. Coke gas forms a main refinery gas source (after dust removal, COS conversion and amine treating for H₂S removal).

Example plants

These systems can be found in many cokers.

Reference literature

[146, TWG DE 2012], [168, VROM 1999].

4.7.9 Techniques to prevent emissions to water

This section analyses ways to prevent emissions to effluents. Techniques used in the final cleaning of the waters generated in the coking processes are found in Section 4.24.

4.7.9.1 Treatment of the waste water

In the coking processes, sour water is generated (steam condensate). Consequently, all water from the coking process is sent to the sour water stripper (Section 4.24) before being sent to the waste water treatment plant.

4.7.9.2 Separation of the oil/coke fines from the coke-cutting water**Description**

This technique consists of retrofitting the sump where the oil/coke fines are collected with an inclined plate separator to increase the separation efficiency.

Achieved environmental benefits

Coke fines and water generated from the coke-cutting operation enter a sump settled on the ground where the solids and water are separated by gravity. A refinery study indicated that this technique could prevent over 25 tonnes per year of coke fines entering the sewage system from that separator.

Cross-media effects

Additional oil/coke fines collected by the separator need suitable treatment or should be properly eliminated.

Applicability

The technique is fully applicable.

Economics

The annual cost savings associated with the increased recovery of product (coke) and the reduction in oil/water separation solids was approximately EUR 300 000 (7.5 Mt/yr refinery).

Driving force for implementation

Reduces the coke fines entering the sewage system and improves the maintenance of the sewage system and accordingly the quality of the raw effluents to the WWTP.

Example plants

No information received.

Reference literature

[249, Balik et al.1991].

4.7.10 Techniques to reduce soil contamination

4.7.10.1 Control and reuse of coke fines

Description

Coke fines are often present around the coker unit and coke storage areas. The coke fines can be collected and recycled before being washed to the sewers or migrating off site via the wind. Collection techniques include dry sweeping the coke fines and sending the solids to be recycled or disposed of as non-hazardous waste. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection), which run to a small baghouse for collection.

Achieved environmental benefits

Reduced soil contamination by coke particulates (including metals). Coke fines can be recycled for fuel use or can be sold (e.g. for cement production).

Cross-media effects

Electricity consumption by vacuum ducts/hoses.

Applicability

Fully applicable.

Driving force for implementation

Reduction of soil contamination.

Example plant(s)

The techniques are already in use in US refineries.

Reference literature

[249, Balik et al.1991].

4.8 Cooling systems

The following topics of relevance to refineries are already described and analysed in the Industrial Cooling Systems (ICS) BREF [69, COM 2001]:

- reduction of direct energy consumption,
- reduction of water requirements,
- reduction of entrainment,
- reduction of emissions to water,
- reduction of air emissions,
- reduction of noise emissions,
- reduction of risk of leakage,
- reduction of biological risk.

The description and analysis include an extensive discussion of the environmental benefits of systems, cross-media effects, operational data, applicability and economics. To avoid repetition, therefore, this section on cooling addresses only topics not covered by the ICS BREF.

4.8.1 Segregation of cooling and process waters

Description

Because process waters are normally more contaminated than cooling waters, it is important to maintain the segregation of the two. Only in cases where cooling waters need treatment (recirculation systems) should they be mixed, and then only at the right point (after the primary treatment of the process waters).

Achieved environmental benefits

Segregation reduces the contamination of cooling water by oil coming from other waters. It increases the recovery of oil by the waste water plant.

Cross-media effects

No cross-media effects have been found.

Operational data

No information received.

Applicability

Waste water treatment plants which were originally sized to jointly handle the process water flow and the cooling water flow may have to be modified after segregation in order to efficiently treat the resulting lower and more concentrated effluent.

Economics

Segregation can be very costly in some parts of existing installations.

Driving force for implementation

To prevent the contamination of cooling water by process waters, which are usually more contaminated, and to avoid the dilution of process waters before their treatment. Some of the topics dealing with pollution of water from cooling systems have already been studied in the OSPAR and HELCOM processes (North Sea and Baltic Sea region).

Reference literature

[160, Janson 1999]

4.8.2 Air cooling

Description

See Section 2.8 and the ICS BREF.

Achieved environmental benefits

The major advantage of using air coolers is that no additional medium is required.

Cross-media effects

Air cooling tends to produce more noise than water cooling. Noise production due to an air cooler fan measures 97 – 105 dB(A) at source.

Operational data

A major disadvantage is that normally a larger plot is required when compared to water coolers (5 – 30 m²/MW). It requires electricity but minimal maintenance costs.

Applicability

Air cooling can be sufficient for the cooling needs in some parts of the refinery process. Ambient conditions restrict the temperature levels that can be attained. Climatic conditions (hot climates or temperatures below 0 °C) typically restrict its use. Moreover, air fans cannot be located near buildings because air short-circuiting may occur.

Economics

Air coolers can be expensive. Minimal maintenance costs.

Example plants

Many examples exist in EU refineries.

Reference literature

[69, COM 2001], [169, Bloemkolk et al.1996], [228, TWG 2000].

4.8.3 Prevention of oil leakages into cooling water

Description

Losses of oil through leaks can be minimised through continuous monitoring, associated with a leak detection and repair system (similar to the reference for VOCs in Section 3.26.1.3).

The first step comprises monitoring the cooling water separators for oil build-up. If oil is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings and flow charts are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak.

This technique is better supported and more efficient when oil-in-water monitors are installed at various points in the cooling water system. This allows leaks to be detected rapidly and corrective action taken. For this procedure to be effective, sparing of critical heat exchangers will be required. More information is given in the ICS BREF.

Achieved environmental benefits

Reduction of oil leakages into cooling water.

Driving force for implementation

Detects and corrects oil leakages into cooling water.

Reference literature

[169, Bloemkolk et al.1996], [228, TWG 2000].

4.9 Desalting

4.9.1 Good desalting practices

Description

A short description of desalters can be found in Section 2.9. Several good desalting designs have been included in this section and include:

1. multistage desalters and the combined use of AC and DC fields providing high desalting efficiencies as well as energy savings;
2. recycling, in multistage desalters, part of the brine effluent water of second stage desalters to the first stage, minimising the wash water quantity;
3. use of a low-shear mixing device to mix desalter wash water and crude;
4. avoiding turbulence in desalter vessels by using lower water pressure.

Achieved environmental benefits

Increased efficiency of desalters can reduce fresh wash water usage. Another environmental benefit could be energy savings, due to a more efficient electrical field.

Operational data

Two-stage processes achieve 95 % or better efficiency (more than 95 % of the salts/solids are removed from the crude oil). This high efficiency provides process benefits, as there is less corrosion in the topping units and less catalyst deactivation, e.g. by sodium.

Applicability

Two-stage or even three-stage desalting is used either if the downstream process salt specification is very stringent or to prevent process upsets and to ensure functionality (e.g. when heavy residues are processed further in catalytic conversion processes).

Driving force for implementation

Increase the efficiency of the desalting process.

Reference literature

[164, Noyes 1993], [207, TWG 2001], [221, Italy 2000].

4.9.2 Enhance the oil/water separation before discharge to the waste water treatment plant

Description

Techniques that may be applied are the following.

- Transfer of the water effluent from desalting units to a settling drum where a further separation of oil and water can be achieved. The oil can be directly recovered in the slop system.
- Choice of optimum interface level controllers. As a function of specific gravity and range of crudes processed, it is possible to consider the most accurate level sensors among displacers, capacitance probes or radio wave detectors. The accuracy of interface level control is fundamental for the good operation of a desalter.
- A good improvement in oil/water separation can be achieved using ‘wetting’ agents, whose aim is to de-oil the solid contaminants that are usually responsible for a significant entrainment of oil in the water.
- Use of non-toxic, biodegradable, non-flammable specific demulsifying chemicals to promote coalescence of the water droplets.

Achieved environmental benefits

The systems described above enhance the oil/water separation, reducing the charge of oil to the waste water treatment and recycling it to the process, as well as reducing the oily sludge generation (see Section 4.9.3). With the application of the first technique mentioned above, some 10 – 20 % less oil is sent to the API separators. The second one can separate off some 5 – 10 % oil from the water phase.

Cross-media effects

Some of the techniques proposed require the application of chemicals.

Applicability

Fully applicable.

Driving force for implementation

Enhance the oil/water separation.

Reference literature

[221, Italy 2000].

4.9.3 Enhance the solid/water-oil separation

Description

Solids entering the crude distillation unit are eventually likely to attract more oil and produce additional emulsions and sludges. The amount of solids removed from the desalting unit should, therefore, be maximised. Thus the objective is to minimise solids leaving the desalter with the crude oil. A number of techniques can be used to accomplish this.

- Use low-shear mixing devices to mix desalter wash water and crude oil.
- Use low-pressure water in the desalter to avoid turbulence.
- Replace the water jets with mud rakes. They cause less turbulence when removing settled solids.
- The water phase (suspension) can be separated in a pressurised plate separator. Alternatively, a combination of a hydrocyclone desalter and a hydrocyclone de-oiler can be used.
- Evaluate the effectiveness of a sludge wash system. The sludge washing is a batch operation meant to stir the water phase in the desalter to suspend and remove the solids accumulated on the vessel bottom. This cleaning operation increases the efficiency of desalters during a normal run, particularly for long cycle runs.

Achieved environmental benefits

With the application of the techniques mentioned above, the content of oil in the generated sludges can be decreased and the separation of the sludges from the water phase can be enhanced.

Cross-media effects

The application of these techniques increases the sludge generation within the refinery. At a bottoms sediment content of the crude of 0.015 % w/w, theoretically 1 500 t/yr sludge can be collected in a 10 Mt/yr refinery.

Applicability

Where bottoms, sediments and water are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids.

Driving force for implementation

Enhances the separation of the oil and water phase by the removal of solids accumulated in the bottom of the desalter vessel.

Example plants

Desalters with desludging facilities are common. Atmospheric residue desalters are scarce, but their number is increasing with the increasing complexity of refineries with respect to residue conversion. In a few refineries, desalters have been equipped with a bottom flushing system (see Figure 2.11).

Reference literature

[221, Italy 2000].

4.9.4 Reuse of water for the desalter**Description**

The desalting process plays an important role in the waste water management of a refinery (see Section 4.15.4). The water used in other processes can be reused in the desalter. For instance, if stripped sour water is used as desalter wash water, the ammonia, sulphides and phenols that it contains can be reabsorbed by the crude to some extent.

The following process water streams can be suitable for use as desalter wash water.

- The accumulated water in the crude distillation unit overhead drum, usually 1 – 2 % w/w on crude feed from steam injection.
- The (unstripped) steam condensates from the light and heavy gas oil dryers and the vacuum distiller overhead (about 3.5 % w/w on feed).
- Stripped sour water and also other solid-free process water streams. Scrubber or quench water is dirty and requires oil and solids separation prior to biotreatment and/or reuse as desalter wash water. The sour water is routed to and stripped in a sour water stripper prior to reuse and/or final purification in effluent water treatment facilities.

Achieved environmental benefits

By using the water in this way, the refinery could reduce the hydraulic loading to the waste water treatment units and reduce the consumption of water.

Cross-media effects

Recycling of water streams that may form emulsions needs to be avoided, because it results in deterioration of the oil/water phase separation in the desalter, which in turn leads to excessive oil carry-over to water. High total dissolved solids (TDS) streams should not be used as desalter wash water, due to the reduced driving force to extract salt from the crude into the water.

Applicability

Examples of effluents that may form emulsions in the desalter are: bitumen blowing units, hydrocrackers, cokers (fines can stabilise emulsions), other deep conversion facilities (insoluble metal sulphides that can stabilise emulsions) and HF alkylation units (corrosive fluoride deposits). The possibility to reuse desalter water as desalter wash water is fully applicable to new refineries but more difficult to apply in existing refineries.

Economics

The costs of collecting, treating, pumping and piping these waters need to be considered.

Driving force for implementation

The refinery could reduce the hydraulic loading to the waste water treatment units and reduce the consumption of water.

Reference literature

[155, API 1993], [207, TWG 2001].

4.9.5 Stripping of the desalter brine

Description

This technique consists of stripping desalter brine for hydrocarbons, sour components and ammonia removal before sending brine to waste water treatment. Recovered hydrocarbons can be blended with several refinery streams. Acid injection can also be employed to enhance the stripping of oil from emulsions.

Achieved environmental benefits

Reduction of the hydrocarbon, sulphur or ammonia (depending on pH range) content of the waste water generated within the desalter. For example, benzene emissions can be reduced by 95 %.

Cross-media effects

This technique consumes steam, added acids, and other chemicals.

Applicability

Pretreatment of desalter brine is normally applied when processing a very heavy crude.

Operational data

In one 8.7 Mt/yr refinery, a waste water flow in the crude unit of 1.3 m³ per minute containing 90 kg/day of phenols is produced. The water discharge from the desalters contains a maximum of 20 ppm benzene, and the quantity of desalter wash water is equivalent to 4 – 8 % v/v of the crude charge. The discharge from the stripper bottoms, with benzene levels in the 20 ppb range, is then routed to the waste water treatment system. A brine de-oiling vessel is installed ahead of the stripping column to decant any free oil from the desalter. It is reported that in refineries, with this system, 90 % of the phenols can be reduced.

Economics

No information received.

Driving force for implementation

This technique allows the reduction of waste water benzene, thereby reducing VOC emissions of benzene in the WWTP.

Example plants

No information received.

Reference literature

[155, API 1993], [164, Noyes 1993].

4.10 Energy system

As mentioned in the Scope, this document does not analyse energy production techniques that use conventional fuels. In other words, emission, consumption, cross-media effects, etc., related to commercial fuels (natural gas, fuel oil, etc.) can be found in the LCP BREF [7, COM 2006].

The energy system is an important activity from the environmental perspective. Although heat-producing plants are an essential and integral part of most refining processes, the systems tend to be very similar and they are therefore dealt with in this horizontal section. This section includes a detailed analysis of the energy systems that are specific to refineries, i.e. only energy technologies that run (partially or totally) on refinery fuels. When a refinery uses a commercial fuel that can be found on the open market (e.g. natural gas, fuel oil) the emission levels that can be achieved by a certain energy technique (e.g. gas turbines, boilers) are found in the LCP BREF [7, COM 2006]. Techniques to reduce the energy consumption of a process or activity are addressed in each of the other sections of this document because the reduction of energy consumption is considered an environmental benefit. However, issues such as how the energy system can be integrated within a refinery and how the different processes/activities may share energy are addressed in this section.

Combustion improvement campaigns, the installation of alternative concepts (gas turbines, CHP, expanders, improved heat integration) and a switch to cleaner-burning fuels are some examples of techniques to consider in the determination of BAT. For example, a switch from liquid refinery fuel to natural gas as refinery fuel will reduce not only SO₂ emissions, but also particulates (including metals) and NO_x. All measures to reduce energy consumption will result in a reduction of emissions to air including CO₂. When end-of-pipe techniques to abate emissions lead the operator to higher energy consumption and increase of CO₂, this is addressed as a cross-media effect. This section has therefore been structured into four blocks of techniques. The first one includes the energy management systems, including general techniques to reduce energy consumption. The second one includes techniques to consider in the selection and cleaning of fuels that can be used in the refinery. The third block contains the techniques for energy production that can provide a good environmental performance using the different types of fuels as well as the utilities needed to run these techniques. The last block (4.10.4 to 4.10.6) includes the abatement techniques to control air emissions that are applicable to energy systems.

Table 4.35 summarises and shows the main impacts which may be connected to the techniques that have been considered in this section.

Table 4.35: Possible effect of the techniques to consider for the determination of BAT in the energy system on main pollutants emissions

| Section | Techniques to consider in the energy system | CO ₂ (*) | NO _x | PM (**) | SO ₂ | Waste water | Residue | Energy |
|---------|---|------------------------|-----------------|------------|-----------------|-------------|---------|--------|
| 1 | Energy management | ↓ | ↓ | ↓ | ↓ | | | ↓ |
| 2 | Refinery fuels: types and cleaning | ↑ | ↓ | ↓ | ↓ | | ↓ | ↑ |
| 3 | Energy production techniques | ↓ | | | | | | ↓ |
| 4 | Nitrogen oxide abatement techniques | ↑ | ↓ | | | | | ↑ |
| 5 | Particulate abatement techniques | ↑ | | ↓ | | ↑ | ↑ | ↑ |
| 6 | Sulphur oxides abatement techniques | ↑ | | | ↓ | ↑ | ↑ | ↑ |

NB: ↓Reduction ↑Increase

(*) CO₂ emissions depend on the type of energy used but are generally expected to follow energy variations.

(**) PM for total particulate matter, without specification of size.

4.10.1 Energy management

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The general aim is to continuously match the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This section should be seen as an integration of all techniques proposed below, since an increase in the energy efficiency of a refinery can be achieved through energy conservation techniques and heat integration/recovery techniques.

4.10.1.1 Energy efficiency management

4.10.1.1.1 Increasing energy efficiency

Description

The continuous matching of production and consumption at the lowest cost is to be performed at all organisational levels and to be assured at the highest management level. This energy management may be included in the site proper management system. In principle, the ISO 14000 system series or EMAS [215, Demuyneck 1999] and EN ISO 50001 on energy management systems provide an adequate framework. In order to ensure continuous improvement, formal reporting of energy consumption data to the authorities can be instigated. Energy audits are part of such a system and it is further recommended that, in the pursuit of continuous improvement, refineries learn from best practice by participating in ranking/benchmarking activities. An annual investment plan on energy consumption reduction is also to be included as a technique to consider in the determination of BAT.

Another way to match production and consumption is to try to improve the energy intensity within the refinery. More efficient refineries make better use of the energy produced within the refinery. To evaluate this, several methodologies exist, including the Solomon energy efficiency index (the most detailed one), specific energy consumption, and (less accurate and more simple) the index relating the energy consumption to the amount of feedstock processed (methods described briefly in Section 3.10.1). Solomon data are also available in that section. Solomon data are available in a form that only makes sense in its context, and one needs to understand certain underlying (benchmarking) concepts that are proprietary to Solomon.

Techniques to increase energy efficiency are available in the next sections of this chapter.

Achieved environmental benefits

An increase in the energy efficiency of a refinery has a direct impact on reducing air emissions and indirectly on the generation of waste water and waste. Lower consumption of fuels or more energy conservation increase the likelihood that the refinery gas supply will be sufficient for the whole refinery.

Cross-media effects

Some difficulties have been identified in the collection of Solomon energy intensity data from refineries. The main reason is that the figures are considered confidential by both refineries and the provider of the market study (Solomon Associates). Furthermore, Solomon Associates has not provided the TWG with data on the methodology used to calculate the figures. Moreover, it was identified that not all refineries participate in this benchmarking exercise, often for different reasons (e.g. cost, confidence in their figures not being high), and not all refineries participate every year.

Applicability

Fully applicable. The wide range of energy consumption in refineries means that in certain refineries, a considerable reduction in energy consumption can be realised. A concerted and well-managed effort based on an integrated approach in reducing energy use, improved

operations, good housekeeping, adequate management and selective investment are good practices that are worth highlighting in this context.

Economics

Energy consumption may account for some 50 – 65 % of the total operating cost of refineries (50 % is the typical value for US operating costs on energy, 65 % is reported for some EU countries in the refining sector). As a consequence, a reduction in the energy consumption or an increase in the refinery efficiency reduces the total operating cost.

Driving force for implementation

Increasing the energy performance of the refinery is typically done because this reduces their operating cost.

Example plants

Many refineries have installed an energy management system; they issue annual reports on energy consumption performance and participate in benchmarking of energy consumption. Worldwide market studies of a wide variety of refineries (configurations/capacities) on the basis of Equivalent Distillation Capacities have proven useful in helping refineries compare their performance.

Reference literature

[68, Worrell et al.2005], [77, REF TWG 2010], [168, VROM 1999], [228, TWG 2000].

4.10.1.2 Heat integration/recovery techniques

4.10.1.2.1 Design techniques

Description

Actions that can be taken to improve integration and recovery of heat and increase efficiency are addressed as a general matter in the Energy Efficiency (ENE) reference document [66, COM 2009]. More specifically, techniques applicable to refineries include (non-exhaustive list):

- General measures to reduce energy consumption, such as optimised heat integration and improved furnace efficiency, combined with computer-controlled combustion. This will lead to lower fuel consumption per tonne of crude processed.
- Installation of waste heat boilers in heaters.
- Installation of expanders/power recovery, e.g. in FCC unit (see Section 2.5).
- Expanded heat exchanger areas in which cold streams are preheated by warm product streams directly from processes.
- Direct feed of ‘semi-products’ to processes without cooling and storage. It is always useful, from an energy conservation point of view, to recover the waste heat of hot products of the crude distillation unit, for instance, by later feeding them directly to the downstream units, rather than cooling them for storage and later feeding the downstream units from tankage.
- Balancing of vapour and refinery fuel gas systems.
- Optimisation of energy production (see Section 4.10.3).

Achieved environmental benefits

Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled. In a refinery, it is important to maximise heat integration in a plant to minimise heating and cooling duties. This way, substantial amounts of products can be sold instead of

being burnt. Heat integration/recovery techniques directly result in lower emissions of CO₂, NO_x, particulates and SO₂ (see Section 3.10.3 for air emissions from the energy system).

Cross-media effects

The interchange of heat between processes implies the transfer of disturbances from one process to another. This can affect safety, so stability control systems may be required.

Applicability

Waste heat is abundant at refineries, and so is low/medium-pressure, low-temperature steam. Any effort to recover waste heat as low-pressure/low-temperature steam is pointless if there is no additional use for the extra steam produced. Options for using that heat need to be carefully quantified and qualified. Heat exchangers require space. The identification and use of opportunities or synergy for sharing use of energy outside the refinery is sometimes difficult and requires finding partners.

Economics

It makes economic sense to maximise heat integration in a plant, and as a result minimise heating requirements and the cooling system burden. Heat integration/recovery offers an opportunity for energy cost savings (50 % of total operating cost of refineries), but the cost of heat exchangers and piping needs to be considered when heat integration is analysed.

Table 4.36 gives various examples of investments for increasing heat exchange surface areas ('add-ons') of existing units and, when available, related payback times.

Table 4.36: Examples of investments for increasing heat exchange reported in EU refineries

| Ref (¹) | Type of units | Energy recovery | Investment cost (EUR) (year) | Payback time (years) |
|-------------------------|--------------------------|-----------------|------------------------------|----------------------|
| [14] | Atmospheric distillation | 10 t/h of steam | 1.2 million | - |
| [26] | Debutaniser overhead | 5.3 MW | 200 000 (2003) | <1.5 |
| [39] | Diesel hydrotreating | 2 000 TEP/yr | 2.5 million (2006) | 6 |
| | Diesel hydrotreating | 400 TEP/yr | 400 000 (2006) | 4 |
| | Crude oil distillation | 6 600 TEP/yr | 3 million (2006) | 6 |

(¹) Site Questionnaire reference number.

Driving force for implementation

Cost savings by reduction of the fuel consumption.

Example plants

Techniques are widely applied in refineries.

Reference literature

[66, COM 2009], [160, Janson 1999], [168, VROM 1999], [207, TWG 2001].

4.10.1.2.2 Process control and maintenance techniques

4.10.1.2.2.1 Steam management and reduction of steam consumption

Description

Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. Steam used for mechanical and/or electrical energy generation and heating is usually recovered as condensate in the HP-, MP-, and LP-condensate systems and collected in the condensate storage tank. Several techniques can be implemented for optimising the use of steam and reducing steam consumption.

- Reducing the amount of steam stripping when not strictly necessary is not only part of a sound energy management, but also an option to reduce the generation of waste water. Stripping steam is normally used to meet flash point specification and to improve front end fractionation and yields distribution. In order to reduce the sour water loads to SWS and reduce chemical treatments in the overhead systems, an option would be to strip sidedraw products, particularly the lighter cuts, using reboiled sidestrippers instead of steamed strippers. However, the majority of steam is used to strip the column bottom, which could not be reboiled by any other means, so the reduction of condensed steam would be limited anyway; besides, the stripping is far better under vapour stream than under reboiling conditions, because the more volatile fraction distillates off.
- Where inert gas such as N₂ is available at an economic price, it can be an alternative to steam for stripping operations, especially for the lighter ends.
- Optimising steam production can also be achieved by waste heat recovery in waste heat boilers (WHB or CHP) from hot flue-gases (e.g. stacks) and hot product streams (related to the techniques shown in Section 4.10.1.2).
- Some sites report interesting initiatives related to systematic programmes for the verification of the very large number of steam condensate drain valves which are usually installed in refinery sites. These programmes consist of the ranking of all valves with regard to induced steam consumption, and the evaluation of all critical valves made from the process and economical points of view. Activities for leakage detection and repair are associated with the programme ('steam traps').

Achieved environmental benefits

Reducing steam consumption reduces the overall energy consumption, and minimises condensates, with a positive impact on waste water generation. The reduction of energy use in steam production will lead to a reduced energy requirement and therefore to lower emissions to air.

Cross-media effects

None in particular.

Operational data

On a French site, a 'steam trap' programme including the systematic mapping of drain valve systems was undertaken in 2008 and covers 20 000 pieces of equipment. At the time of writing (2010), around 30 tonnes of steam per hour have been saved since the programme started. The same approach has been followed on a British site, involving, since 2008, a dedicated team which has managed to reduce steam losses to atmosphere by around 50 000 t/yr.

Economics

The programme mentioned corresponds to a total annual investment estimated at EUR 450 000.

Driving force for implementation

Environmental driving force aimed at energy saving and related decrease of air and water emissions.

Example plants

Applications are found in some refineries.

Reference literature

[221, Italy 2000], [Questionnaires n° 16 and 45].

4.10.1.2.2.2 Other techniques

- Use of high-efficiency pumps and compressors.

- Use of heat pumps.
- Decreased film temperature and increased turbulence on heat transfer surfaces.
- Application of advanced process control to optimise energy use.
- Insulation of buildings and process units (minimisation of heat losses by thermal radiation).
- Optimisation of recycle gas rates, operating temperatures and pressures and steam pressure levels.
- Minimisation of slops production and their necessary reprocessing.
- Keeping heat exchanging surfaces clean or cleaning them regularly (good housekeeping - see Section 4.10.3.1)
- Repairing leaks and leaking steam traps (see Section 4.10.1.2.2.1).
- Increasing heat exchanger surface areas of new sections of existing plants ('add-ons'). In the cases where more add-ons have been added to an existing plant: re-routing of intermediate process streams and redefinition of the number of steam pressure levels and steam duties.

4.10.2 Refinery fuels: types and cleaning

As mentioned above, this document offers a detailed analysis only of refinery fuels produced in the refinery. Whilst the use of marketable fuels such as LPG, commercial fuel oil and gas oil in refineries is a technique to consider that may be included in this chapter of the BREF, such use is extensively analysed in the LCP BREF [7, COM 2006], which also gives achievable emission levels using these fuels.

4.10.2.1 Increase the use of gas

Description

An alternative to reducing SO₂, NO_x, CO₂ and metals emissions from a refinery would be to replace or decrease the use of liquid refinery fuel with LPG (often produced on site), refinery fuel gas (produced by some conversion techniques) or natural gas (from external supply). This increase of the use of gas is typically accompanied by a balance and control of the RFG system between suitable pressure limits to give the system flexibility, with RFG make-up available from clean fuels such as LPG or imported gas. In these cases, state-of-the-art controls that optimise the performance of the RFG are necessary.

Achieved environmental benefits

Fired boilers and furnaces generate substantial CO₂, SO₂, NO_x and particulate emissions, particularly when heavy fuel oil is used. Gas-fired boilers generate hardly any dust and low SO₂ emissions when the refinery gases are cleaned in amine scrubbers. NO_x emissions are also much lower than those of oil-fired boilers.

Because of the low SO₂ concentrations in the flue-gases of gas-fired boilers, the emission temperatures at the stack can be lowered to 150 °C (dew point corrosion is less of or no longer a constraint). The lower flue-gas temperature represents a difference in energy efficiency and inherent CO₂ emission reduction.

A full switch to a 100 % gas-fired refinery would drastically reduce SO₂, CO₂ and NO_x emissions. Releases of heavy metals would also be slashed. Furthermore, the use of gas generates very little dust and very low SO₂ emissions, as part of the refinery gases are cleaned in amine scrubbers (see next section). Sulphur emissions are significantly lower when clean refinery fuel gas is used instead of a distillate such as automotive gas oil, i.e. 10 - 20 times better than low-sulphur (1 %) conventional fuel oil.

Gaseous fuels typically release less NO_x per unit of energy compared to liquid fuels, especially liquid refinery fuels. For gaseous fuels, usually only thermal NO_x is relevant; however, NO_x emissions will depend on the gaseous fuel composition. Oil burning normally leads to higher levels of NO_x releases for several reasons, especially due to fuel NO_x arising from the nitrogen content (see Section 4.10.2.3), the need to balance NO_x and particulate releases and the frequent design requirement for firing in combination with gas. More detailed information for achievable emission values can be found in Table 4.39 and Table 4.42.

As a matter of summary, the benefits for a switch to a 100 % gas-fired refinery are given below.

- SO_2 emissions from the energy system will be drastically reduced. These emissions will be very low from the refinery gas, and virtually zero for the natural gas. Contributions to the refinery bubble will be mostly attributed to emissions from other sources (SRU, FCC unit, flares, etc.)
- Particulate emissions including heavy metals will be reduced.
- NO_x levels typically achieved by gas firing will be reduced to levels typically achieved for gas firing for energy production techniques, and consequently other sources such as catalytic crackers will become predominant emitters in the refinery.
- CO_2 emissions reduction is achieved mainly because of the lower carbon content of gas, its higher calorific value and in addition because of a higher attainable efficiency (stack gases can be cooled further).

Cross-media effects

It is acknowledged that the residual fuel replaced by gas results in a further surplus of residue, which has to be considered in any integrated solution for the fuel system of a refinery. Those residual fuels could be burnt improperly outside the refinery, so emissions produced in that way can be seen as merely an emission shift to outside rather than an elimination. Furthermore, the conversion of heavy fractions into light products and the targets for lower sulphur specifications of fuels require considerable extra energy. This will lead to an inevitable increase in CO_2 emissions, unless the CO_2 could be captured.

As a first approximation, NO_x emissions can be magnified by the use of hydrogen, the heaviest gaseous hydrocarbons, and residual fuels containing fuel-bound nitrogen. High-hydrogen fuels result in higher flame temperatures, which typically lead to higher NO_x levels. Although not all the fuel nitrogen ends up as NO_x emissions, the fuel NO_x contributions can range from non-existent, as in the case of natural gas-fuelled equipment, to several times the thermal NO_x contribution of the equipment for refinery fuels. Refinery fuel gas may contain amines (nitrogen compounds) and other compounds. Adjustment factors for NO_x emissions as a function of the bound nitrogen content of heavy fuel oils are available in the literature. A well-recognised reference on this subject is provided by the 'Besluit Emissie-Eissen Stookinstallaties Milieubeheer A' (BEES) guidance document published by the Dutch competent authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed in Figure 4.31.

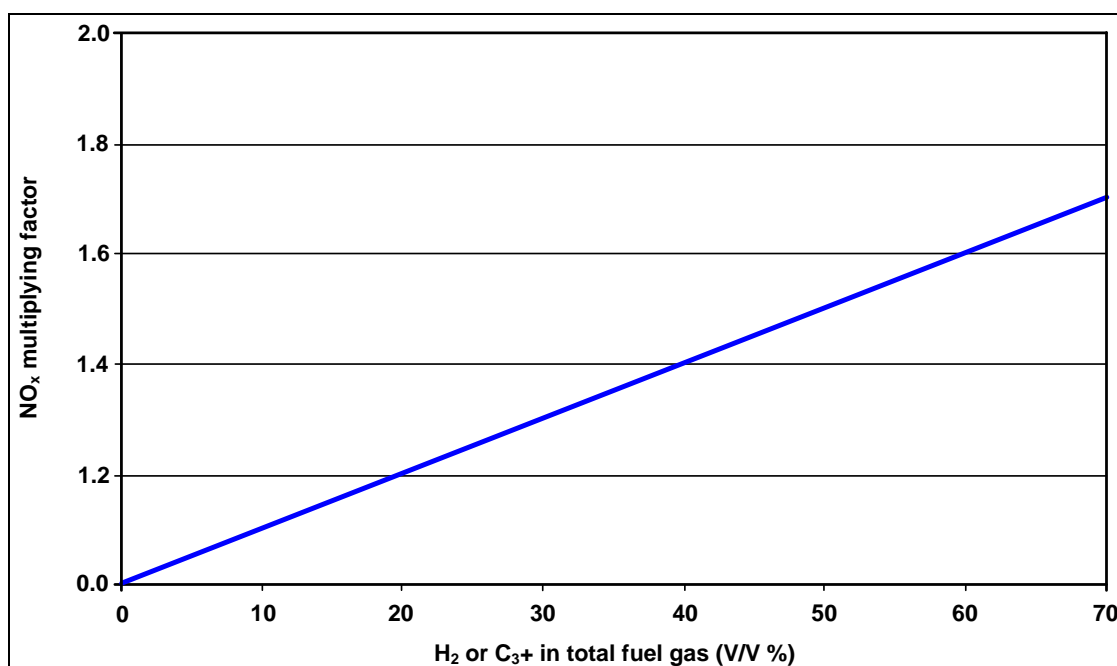


Figure 4.31: Effect of the refinery fuel gas composition on NO_x emissions (applying only to existing installations)

The adjustment factor proposed by the BEES document is made up with the combination of two factors multiplied together. The first accounts for the hydrogen content and the second is attributed to hydrocarbons having a carbon number greater than three.

Nevertheless, a linear relation of NO_x formation with hydrogen content of gaseous fuels cannot be straightforwardly applied: emissions variability is also linked to variation in gas quality and gas quantity and the various types of installations. [267, ECN 2012]

Further information on conversion techniques for heavy fractions to refinery fuel gas can be found in Section 4.10.3.4: the coking sections and the hydroconversion processes sections.

Applicability

The move from liquid to gas fuel would require process upgrades and gas grid connections. Some gases are used locally, i.e. in the process of origin or an adjacent process, but most refineries operate a common RFG mains into which most RFG is fed and transferred to gas users. In a modern refinery, the RFG mains is carefully 'balanced' with respect to supply and demand; necessary flexibility is achieved by control of production (i.e. reformer throughput, LPG evaporation). The relationship with the refinery flare system is important and RFG will normally include gas received from flare gas recovery. It may also release excess gas to flare if the upper pressure limit is exceeded. The application of energy conservation concepts (see Section 4.15.1.2) can help refineries to meet all their needs with refinery gas produced in-house.

The US EPA has recently reached a number of settlement agreements (referred to as Partnership Civil Judicial Settlements, or Consent Decrees) with major companies at the company or site level, in order to eliminate or minimise the use of solid and liquid fuels in all boilers and heaters operated in the refineries [25, Pham et al.2009]. According to these settlement agreements, the use of solid/liquid fuels is only allowed during natural gas curtailment periods.

Nowadays, a number of European refineries have also switched to 100 % gas with similar operating conditions.

Operational data

In Figure 4.32, a very clear correlation is displayed between the part of gaseous fuels burnt in the site energy mix and the specific NO_x and SO_2 emissions achieved by a sample of 55 European refineries during the period 2007 – 2008.

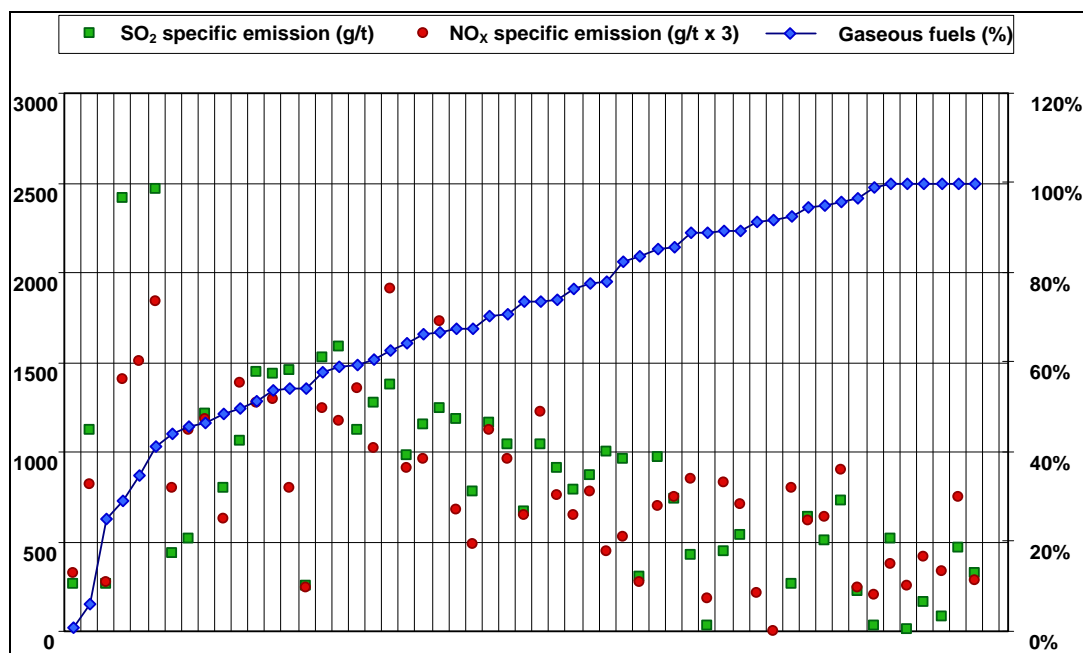


Figure 4.32: Relation between the fuel-mix part and specific NO_x and SO_2 emissions for a sample of European refineries

Figure 4.33 shows the current respective uses of gas and oil in the energy system for a sample of European refineries. From these data, in 2008, the median percentage of gas firing was around 75 % and liquid oil firing close to 25 %. For oil firing, the corresponding average sulphur content was 1.06 %.

This information is consistent with the CONCAWE survey on sulphur dioxide emissions [139, CONCAWE 6/11 2011] showing a decreasing oil use from 28.5 % in 1998 to 19.1 % in 2006, and an average sulphur content of 1.33 % in 2006.

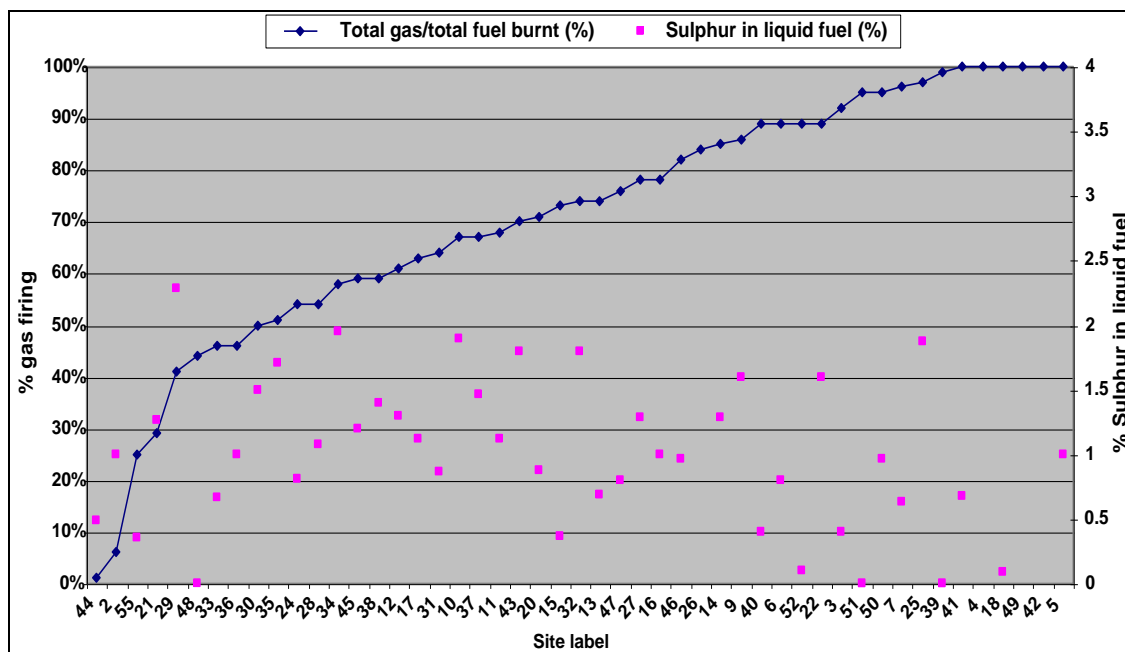


Figure 4.33: Percentage of gas firing and oil sulphur content in 2008 TWG data sample

Economics

The cost of switching to gas can be as high as EUR 30 million per year for a 10 Mt/yr refinery.

For the use of LPG in lieu of fuel oil, the approximate capital cost is small (some reburning) and the approximate operating cost per year is EUR 120 per tonne of fuel (cost differential between LPG and fuel oil). However, operating costs can vary significantly, depending on the season of the year and on the price of LPG on the market.

For the use of natural gas in lieu of fuel oil, the approximate capital cost of installation is around GBP 4 million. The approximate operating cost per year may vary from below EUR 50 per tonne to above EUR 100 per tonne (cost differential between natural gas and fuel oil). Again, operating costs can vary significantly depending on the season of the year and on the market. Cost data for switching to natural gas, from CONCAWE 6/11 presented in Table 4.60 (for comparison with a wet gas scrubber), show a range to consider of 75 – 150 EUR/t per yr of fuel oil equivalent (FOE).

Driving force for implementation

Reduction of CO₂, NO_x, SO₂ and particulate emissions (including metals).

Example plants

In 2008, half of the EU refineries have a share of gas firing (RFG + NG) of more than 75 %.

Very few European sites rely upon more than 25 % of heavy liquid fuels for their own energy supply.

Reference literature

[7, COM 2006], [64, CONCAWE 2010], [168, VROM 1999], [193, BMUJF 1999], [207, TWG 2001], [218, HMIP UK 2000].

4.10.2.2 Cleaning of refinery fuel gas

Description

Some refinery fuel gases (RFG) may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking and all hydrodesulphurising processes). In the latter case, the gas streams are normally treated by amine scrubbing to remove H₂S before being released to the refinery fuel gas system. More information about amine scrubbers can be found in Section 4.23.5.1.

Achieved environmental benefits

As shown in Table 4.80 of Section 4.23.5.1, amine treated refinery fuel gases can be controlled to levels that range, depending on the amine scrubber pressure, from 2 – 15 to 20 – 220 mg H₂S/Nm³. These levels will lead to a range of 5 – 35 mg/Nm³ SO₂ at 3 % O₂ in flue-gases where the upper level of H₂S is 220 mg/Nm³ and taking into account a maximum hydrogen content of 45 % (Source: [36, CONCAWE 4/09 2009]).

Cross-media effects

Possibility of bottlenecking the amine scrubbing system. More information can be found in Section 4.23.5.1.

Operational data

See Section 4.23.5.1. In 2010, the amine cleaning of refinery fuel gases is adjusted to below 25 – 35 ppmv (annual average) in various US refineries [25, Pham et al. 2009] in order to meet the SO_x standards imposed for furnace and boiler emissions.

It should be noted that fuel gas may contain other sulphur compounds such as mercaptans (from thermal cracking processes) or COS (from FCC and flexicoker units, see Section 4.7.8.4) which are not removed by amine scrubbers.

CONCAWE 04/09 identified that the composition of RFG (non-S compounds) influences the concentration of SO₂ measured in the flue-gas. The complete combustion products of a RFG are CO₂, H₂O and SO₂ and N₂ and the remaining O₂ from the combustion air. When SO₂ is measured in the flue-gas, it is done so on a *dry basis*. The volume of *water vapour is removed* and therefore the SO₂ concentration is higher. The RFG comprises mainly hydrogen and light hydrocarbons (C1, C2, C3) and as a consequence water is produced when it is burnt.

This means that, for a fixed concentration of H₂S in the RFG achieved by amine treating and/or blending, a different SO₂ concentration will be measured in the flue due to this formation of water during the combustion depending on the composition of the RFG (non-S compounds).

Applicability

Fully applicable.

Economics

See Section 4.23.5.1.

Driving force for implementation

To reduce the sulphur content of the flue-gas of the refinery.

Example plants

The treatment of refinery fuel gas in amine scrubbers is commonly used in all refineries.

Reference literature

[36, CONCAWE n°4/09 2009], [221, Italy 2000].

4.10.2.3 Hydrotreatment of liquid refinery fuels

Description

The nitrogen, sulphur, particulates and metals contents of the fuel used in refineries are determined by the crude that is used at the refinery and by the process units it has passed through. Liquid refinery fuel streams originate from various processes such as crude distillation units, vacuum distillation, thermal cracking, cat cracking and hydrocracking of residues. Except for the latter, the sulphur content of these residues can only be controlled by feedstock choice. In general, the liquid refinery fuel may comprise one or more of the aforementioned fractions and the sulphur content can vary greatly. Table 4.37 shows the sulphur, nitrogen and metal content of different fractions suitable to be used as liquid refinery fuel.

Table 4.37: Sulphur, nitrogen and metal content of fractions suitable for liquid refinery fuels

| Fraction suitable to be used as liquid refinery fuel | Crude oil origin | S (%) | N (%) | Metal content (%) |
|--|------------------|-----------|-------------|-------------------|
| Atmospheric residue | North Sea | 0.6 – 1.1 | 0.03 – 0.32 | 0.03 – 0.06 |
| Atmospheric residue | Middle East | 2.3 – 4.4 | | 0.04 – 0.06 |
| Vacuum residue | North Sea | 1.1 – 1.8 | 0.18 – 0.58 | |
| Vacuum residue | Middle East | 3.6 – 6.1 | | 0.07 – 0.13 |
| Cracked residue | Middle East | 3.5 – 6.5 | | |

Based on hydrogenation reactions, the hydrotreatment of fuels can reduce the sulphur, nitrogen and metal content of the refinery fractions. The hydrotreatment of liquid fuels can reduce the sulphur content to 0.03 – 1 %. For more information on hydrotreatments, see Section 2.13. This technique is a precombustion operational change, treating the feed before it is used.

Achieved environmental benefits

Feed hydrotreating of fuels reduces the feed nitrogen, sulphur and metals content, which in turn reduces the SO₂, NO_x and particulate emissions. It has been calculated that by switching to fuel oil with a sulphur content of 1 % or less, UK refineries can reduce SO₂ emissions by 19 – 64 %. Another advantage of switching to low-sulphur fuel is that it reduces heat loss to the flue-gas stack (investment in extra heat exchangers or heat exchanger surface to be made) because dew point corrosion is minimised or is no longer a constraint.

Cross-media effects

The hydrotreatment of fuels is a very energy-intensive process that consumes hydrogen and consequently leads to increased CO₂ emissions. Moreover, effluent water and waste (used catalyst) are generated (see Section 3.13).

Operational data

Adjustment factors for NO_x emissions as a function of the bound nitrogen content of heavy fuel oils are available in the literature. A well-recognised reference on this subject is provided by the 'Besluit Emissie-Eissen Stookinstallaties Milieubeheer A' (BEES) guidance document published by the Dutch competent authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES report is displayed in Figure 4.34.

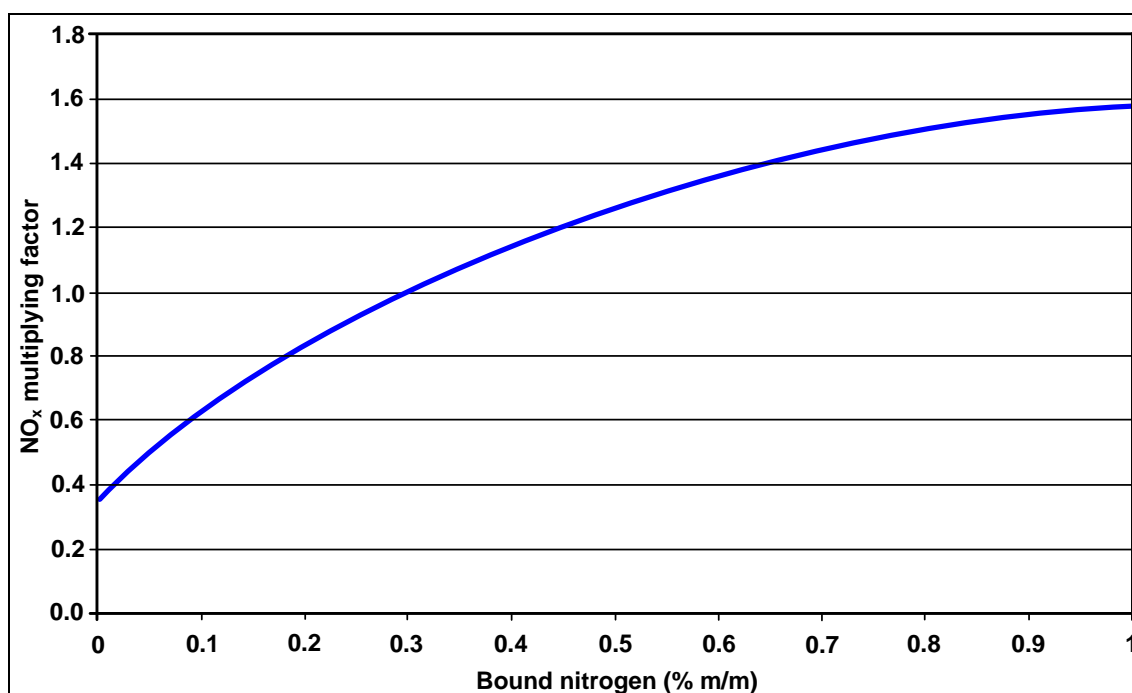


Figure 4.34: Effect of bound nitrogen concentration on NO_x emissions from fuel oil firing

Other information on the performance and consumption of hydrotreatments can be found in Sections 2.13 and 3.13.

Applicability

Fully applicable.

Economics

An intensive hydrotreatment is very expensive, increasing the cost of the liquid refinery fuel. Table 4.38 shows an example of the costs of liquid refinery fuel desulphurisation processes.

Table 4.38: Costs of a liquid refinery fuel desulphurisation

| | |
|-----------------------------|---|
| Capacity of the refinery | 5 Mt/yr |
| Fuels used in the refinery | 120 000 t/yr liquid refinery fuels 180 000 t/yr refinery fuel gas |
| Volume of flue-gas emitted | $1.68 \times 10^9 \text{ Nm}^3/\text{yr}$ |
| Sulphur emission | 5 000 mg/Nm ³ (for liquid refinery fuels with 3 % S) representing 8 400 t/yr (750 mg/Nm ³ with hydrotreatment) |
| Desulphurisation efficiency | Up to 85 % |
| Investment cost (EUR) | 100 – 300 million |
| Operating costs (EUR/yr) | 20 – 50 million |

Driving force for implementation

Optimisation of the refinery configuration.

Example plants

The amount of refinery gas combusted by refineries compared to liquid fuel, in terms of megawatts fired, is typically 60 % refinery gas to 40 % liquid refinery fuel. However, data from the public register for 1996 in the UK show that in some refineries the amount of fuel oil fired approached 60 %.

Reference literature

[36, CONCAWE n°4/09 2009], [151, Sema, Sofres 1991], [168, VROM 1999], [192, Ademe 2001], [218, HMIP UK 2000].

4.10.3 Energy production techniques

All types of energy production techniques found in refineries are included here. However, the emission levels associated with each technique are different from those included in Chapter 3 of this document, because only good performance levels are included in this section. Techniques to prevent emissions from these energy production techniques are also included.

4.10.3.1 Furnaces and boilers

Description

The primary measures considered in this section for furnaces and boilers are given below (see also the LCP BREF [7, COM 2006]):

- Installation of combustion air preheaters, which can increase the furnace efficiency significantly (by more than 5 %).
- Optimisation of furnace operations, and hence combustion efficiency, by an advanced control of the operations variables (air/fuel ratio for the fuel mix, avoiding sensible heat losses by optimising excess air).
- High thermal efficiency heater/boiler designs with good control systems (e.g. oxygen trim).
- Minimisation of heat losses via exhaust gas (e.g. minimisation of heat losses via unburnt gases (H₂, CO) or unburnt residues, i.e. ignition loss).
- Continuous monitoring of temperature and O₂ concentration of flue-gas for combustion optimisation. Monitoring of CO may also be considered.
- Maintaining a high boiler pressure.
- Preheating of fuel charged to the boilers.
- Preheating of boiler feed water with steam (see also Section 4.10.3.2).
- Prevention of the condensation of exhaust gas on surfaces.
- Minimisation of own requirements by high-efficiency pumps, vents, and other equipment.
- Optimisation of combustion conditions.
- Techniques to control CO emissions such as:
 - good operation and control
 - constant delivery of liquid fuel in the secondary heating
 - good mixing of the exhaust gases
 - catalytic afterburning.
- Regular on-line heater hot tube descaling and hot convection cleaning (dry treatment).
- Regular cleaning of heating surface (soot blowing) for liquid fuel or mixed firing.
- Ceramic coatings for process tube protection against oxidation and prevention of scale build-up.
- High emissivity refractories for radiant heat transfer improvement, e.g. by application of ceramic coatings.

Achieved environmental benefits

Table 4.39 to 4.46 provide the achievable emission levels when primary measures are implemented in furnaces and boilers for each air pollutant. Some specific techniques, such as low-NO_x, flue-gas desulphurisation and others are reviewed later in this chapter. Values in the tables are in mg/Nm³, attainable in continuous operation (half-hourly mean values) and are based on a 3 % oxygen volume in the waste gas, except where specified. For gas, the lower values in the ranges given below relate to natural gas firing. Liquid refinery fuel refers to thermal cracked residue, vacuum residue, etc.

Table 4.39: Expected CO emissions from furnaces and boilers with optimal burner and design

| Source | Gas | Liquid refinery fuel (*) |
|--|----------|--------------------------|
| Process furnaces | 5 – 80 | 20 – 100 |
| Boilers | 5 – 80 | 20 – 100 |
| Engines | 10 – 150 | |
| (*) For liquid firing, a concentration below 50 mg/Nm ³ is achievable at temperatures above 800 °C, with sufficient retention delivery and retention time. Source: [228, TWG 2000] | | |

Table 4.40: Expected NO_x emissions from furnaces and boilers with optimal burner and design

| Source | Gas | Liquid refinery fuel | |
|---|---|----------------------|-----------|
| | | 0.3 % N | 0.8 % N |
| Process furnaces | 80 – 120 ⁽¹⁾ | 280 - 450 | 280 – 450 |
| Boilers | 250 in some cases of retrofit in old installations ⁽²⁾ | 300 – 450 | 350 – 600 |
| Engines | 250 – 400 | NA | NA |
| ⁽¹⁾ TWG 2010 data collection (see also Table 4.46 for mixed firing). Expected emissions result from multiple factors, including both burning optimisation and burners design. | | | |
| ⁽²⁾ TWG 2010 data collection questionnaire number 14 (see Table 4.46) | | | |

Table 4.41: Expected particulate emissions from furnaces and boilers with an optimal burner and design

| Source | Gas | Liquid refinery fuel |
|----------------------|-----|----------------------|
| Boilers and furnaces | <1 | 20 – 250 |

Cross-media effects

Air preheating typically increases the production of NO_x. Adjustment factors for NO_x emissions as a function of preheated air temperature are available in the literature. A well-recognised reference on this subject is provided by the 'Besluit Emissie-Eissen Stookinstallaties Milieubeheer A' (BEES) guidance document published by the Dutch authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed in Figure 4.35.

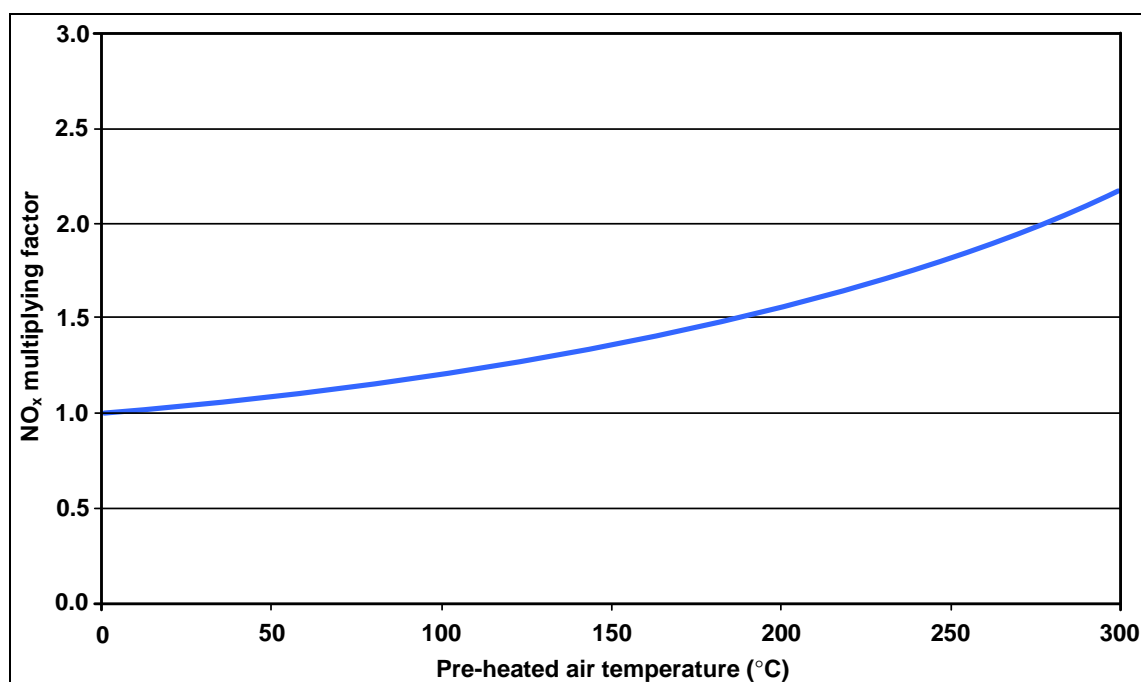


Figure 4.35: Effect of air preheating on NO_x emissions for fuel gas firing (applying only to existing installations)

This factor is applied directly for units fired with refinery fuel gas and addresses only the increase in thermal NO_x production. In the case of fuel oil or mixed liquid/gas fuel firing, this factor should be applied after first adjusting the bound fuel nitrogen to zero (see Figure 4.34 in Section 4.10.2.3), in order to avoid double counting the NO_x increase due to the fuel nitrogen conversion.

Operational data

Direct gas-fired heaters and boilers normally achieve thermal efficiencies of over 85 %. If air preheating is applied and the combustion products (flue-gas) are cooled close to their dew point, the thermal efficiency can be as high as 90 – 93 %.

An average fuel reduction of around 3 % has been achieved by retrofitting ceramic coatings on existing process furnace tubes (e.g. on catalytic reforming and vacuum distillation furnaces). A 2 % reduction was also observed after retrofitting high emissivity ceramic coatings on existing refractories of steam reformer furnace walls. In both cases, the related reduction of NO_x emissions could be estimated to be 30 % for furnaces equipped with conventional burners, and 5 % for those equipped with low-NO_x burners.

Applicability

Most of the techniques mentioned in this section are generally applicable. However, some restrictions to applicability for retrofitting existing units are to be taken into consideration. In the particular case of ceramic coatings, retrofitting this technique to furnaces fired with 100 % heavy liquid fuels is not advised.

Economics

The retrofitting of ceramic coatings on tubes and refractory walls of a 0.5 Mt/yr catalytic reforming furnace and a 2.1 Mt/yr vacuum distillation furnace costs around EUR 0.2 – 0.4 million per furnace (2004). The related payback time was estimated at six months for the increased productivity (capacity and/or cycle run length) and at two years as far as energy consumption is strictly concerned.

Driving force for implementation

Reduction of energy consumption and related emissions from processes requiring heat or steam production.

Example plants

All techniques mentioned in this section are widely used in numerous process furnaces operated worldwide. In the particular case of tube and/or refractory ceramic coatings, more than 30 process furnaces have been treated since 2000 in Australia, Canada, Germany, Italy, Mexico, Japan and the US.

Reference literature

[7, COM 2006], [36, CONCAWE n°4/09 2009], [151, Sema, Sofres 1991], [167, VDI 2000], [168, VROM 1999], [177, WRA 1999], [193, BMUJF 1999], [207, TWG 2001], [221, Italy 2000], [Questionnaire n° 25].

4.10.3.2 Gas turbines

Description

A description of gas turbines can be found in the LCP BREF [7, COM 2006]. A brief description can also be found in Section 2.10. Some techniques that can be applied to gas turbines in order to reduce air emissions are listed below:

- steam injection;
- gas turbines with exhaust gas as combustion air;
- optimised transformation of steam into electrical energy (highest possible pressure difference in the steam turbine, generation of steam with high temperature and pressure, multiple reheating of the steam);
- other primary techniques such as dry low-NO_x burners covered in Sections 4.10.4.1 to 4.10.4.3;
- use high-efficiency turbines by, for example, optimisation of the design of the turbines, reducing to as low as is technically feasible the outlet steam pressure in the back-pressure turbine.

Achieved environmental benefits

Table 4.42 summarises the emission levels that can be achieved with the application of the primary measures for gas turbines.

Table 4.42: Expected air emissions from gas turbines with primary techniques

| Pollutant | Gas ⁽¹⁾ (mg/Nm ³) | Liquid refinery fuel ⁽²⁾ (mg/Nm ³) |
|---|---|--|
| CO | 5 – 100 | <50 |
| NO _x (as NO ₂) at 15 % O ₂ | 20 – 50 (new turbines) 20 – 90 (existing turbines ⁽³⁾) | 200 (with water injection) |
| Particulates (at 15 % O ₂) | | <5 – 30 with abatement |
| ⁽¹⁾ The lower range relates to natural gas firing. ⁽²⁾ Gas oil/jet oil. ⁽³⁾ Lower range with dry low-NO _x burners (DLN). Source: [7, COM 2006] | | |

Additional measures to abate NO_x emissions as low as 65 mg/Nm³ (15 % O₂) with, e.g. SCR, are also possible for existing gas turbines. See Section 4.10.4.7.

Environmental performance and operational data

Table 4.43 shows the achieved emissions values from a sample of gas turbines operated in some European refineries and using, at minimum, one of the techniques to reduce NO_x emissions as

described previously. These data show the minimum and maximum monthly concentrations of NO_x (at 15 % O₂ level) observed from continuous monitoring for a number of refinery gas turbines in Europe, the currently applied techniques and the operational conditions. [145, TWG CONCAWE 2012]

Table 4.43: Emissions of NO_x from gas turbines - Data from a sample of European refineries

| Refinery Code | NO _x Min. monthly | NO _x Max. monthly | Techniques in place – Operational conditions |
|---|------------------------------|------------------------------|--|
| J2 | 40 | 70 | Steam injection, RFG, syngas, NG mixture changes |
| P | 52 | 75 | Steam injection, fired on FCCU off-gas |
| J1 | 40 | 80 | Steam injection, RFG, syngas, NG mixture changes |
| F | 85 | 95 | Steam injection, firing NG during data period |
| K | 80 | 110 | Steam injection peak shaving (high load factor change) |
| S | 95 | 110 | Four small 6 MW turbines fired on RFG/NG |
| M | 110 | 120 | SCR fitted. RFG-fired |
| H | 85 | 135 | Steam injection varied over period. Fired on NG/RFG/middle distillate |
| V | 130 | 160 | Steam injection, NG (96 %) + RFG blend – the NO _x emission is affected by the crude being processed |
| W1 | 230 | 340 | Partial load operation: 150 mg/Nm ³ |
| NB: All concentration values expressed as mg/Nm ³ at 15 % O ₂ content. Source: [145, TWG CONCAWE 2012] | | | |

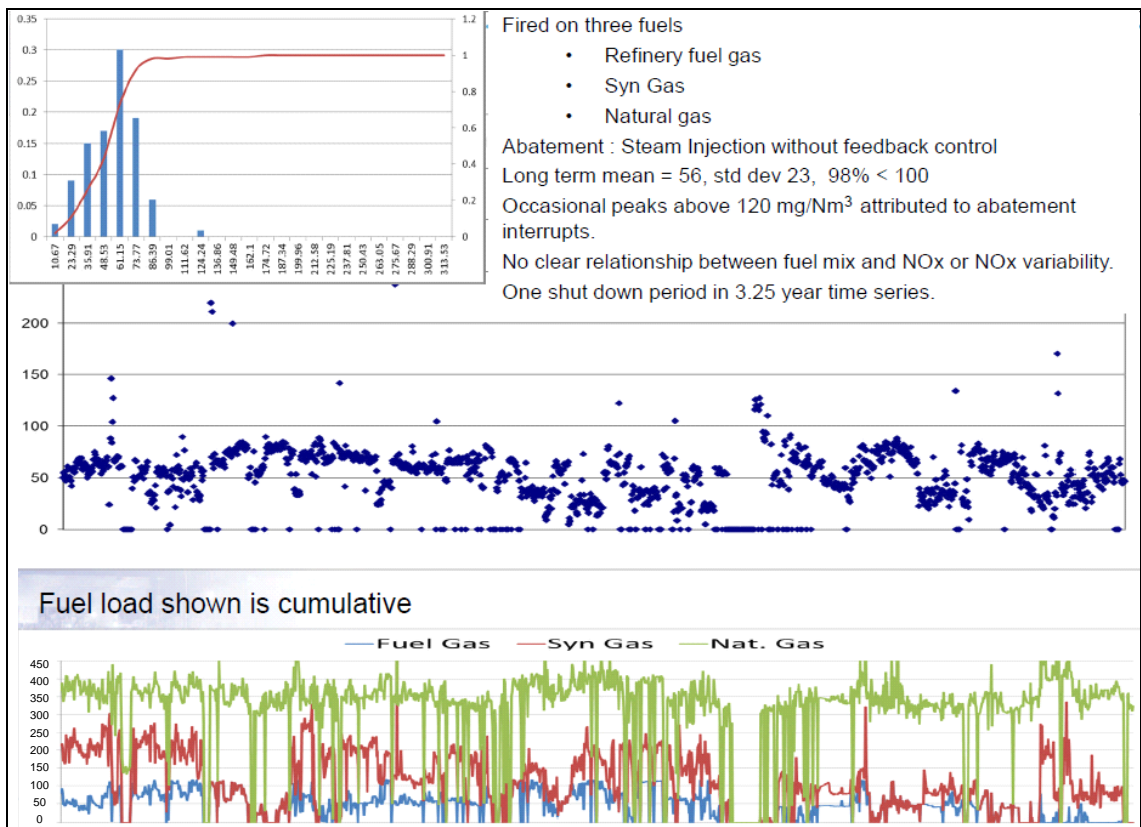


Figure 4.36: Daily variations of emissions to air from a gas turbine using three fuels (example from refinery J-GT A -170 MW)

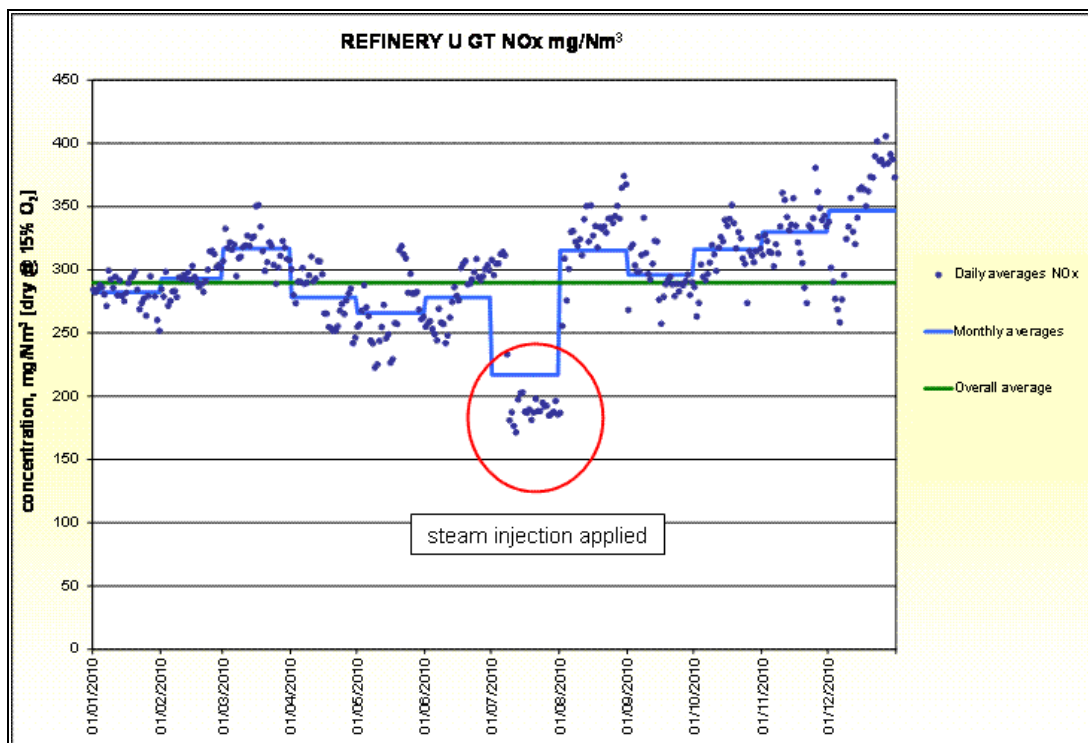


Figure 4.37: Effect of the application of steam injection to a gas turbine operating with a mixture of natural gas and refinery fuel gas (75 % RFG)

Cross-media effects

Steam injection typically generates higher emissions of CO and hydrocarbons. Steam should be produced if it is not available in the refinery.

Applicability

Fully applicable. Steam injection is particularly applicable where high-hydrogen (H₂) content fuels are used. [145, TWG CONCAWE 2012], [266, Chiesa et al. 2003].

Economics

Steam injection applied to an 85 MW_e output turbine. Uncontrolled NO_x emissions of 500 mg/Nm³ at 15 % O₂ down to 50 – 80 mg/Nm³ at 15 % O₂. Investment cost (1998): EUR 3.4 million (including cost of steam production). Operating cost: EUR 0.8 million (excludes capital charge).

Driving force for implementation

Process technique used for the production of electricity.

Example plants

Many examples exist in refineries. A number of refineries have or are currently installing combined cycle gas turbines (CCGT) designed to produce steam and power for the refinery. This is usually done to replace, in whole or part, an old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators. A recent example (December 2011) for upgrading six gas turbines at Qatargas LNG plant (Qatar) shows a dry low-NO_x system designed to achieve emissions levels of 25 ppm (<50 mg/Nm³).

Reference literature

[7, COM 2006], [145, TWG CONCAWE 2012], [151, Sema, Sofres 1991], [166, CONCAWE 1999], [168, VROM 1999], [266, Chiesa et al. 2003].

4.10.3.3 Cogeneration plants (CHP)

Description

A brief description can be found in Section 2.10.

Achieved environmental benefits

For the refinery/other power generators (OPG) combination, energy consumption and CO₂ emissions will be reduced by the application of the CHP concept. At the OPG, fuel consumption and all related emissions will be reduced but, at the refinery, fuel consumption and emissions may increase. A refinery that generates its own steam and electricity (no import from the OPG) can benefit from (enhanced) cogeneration. In these cases, the environmental benefits include reduced fuel use and its related emissions.

Cross-media effects

No cross-media effects have been detected.

Operational data

Most turbines require a particularly stable mix of fuel in order to be sure of flame stability and are basically designed to burn natural gas. Refinery fuel gas components can vary considerably, especially when surplus hydrogen is produced, such as when a hydrotreatment unit is temporarily shut down, resulting in excess hydrogen being sent to the fuel gas system. However, these problems can usually be overcome, up to a limit of about 70 % hydrogen in the fuel.

Applicability

Generally applicable. The steam and power cogeneration concept can be also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high-pressure

steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Driving force for implementation

For the production of steam and power to be used within or outside the refinery.

Example plants

A number of refineries have, or are currently installing, a combined cycle gas turbine (CCGT) or Combined Heat and Power (CHP) plant, designed to produce steam and power for the refinery. This is usually done to replace, in whole or part, an old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators.

Reference literature

[168, VROM 1999].

4.10.3.4 Gasification of heavy oils or coke (IGCC)

Description

Integrated gasification combined cycle (IGCC) is a technique whose purpose is to produce steam, hydrogen (optional) (see Section 2.14) and electric power from a variety of low-grade fuel types with the highest conversion efficiency possible. More information can be found in Section 2.10.

Achieved environmental benefits

Syngas produced in this process has a sulphur content of 0.01 – 0.05 % and could be used as refinery fuel gas for hydrogen, fuel or chemical production. Water containing the soot particulates is filtered and the filter cake is subjected to a controlled burning process. The process is, in principle, autothermic; the heat of combustion being sufficient to evaporate the moisture content of the filter cake.

The IGCC is a highly integrated and efficient process which can supply power, hydrogen and steam. Furthermore, it offers, in principle, an acceptable outlet for heavy residues and feedstocks or even refinery sludges, provided the latter are less than 1 % of feed. Hot gas clean-up systems have the potential to increase system efficiency and lower system costs. The achieved emissions to the atmosphere from that system are: SO₂: 50 mg/Nm³, NO_x: 65 mg/Nm³ at 3 % O₂, particulate matter: 5 mg/Nm³ and carbon monoxide: 10 – 30 mg/Nm³.

The emissions from the IGCC show a significant decrease compared with conventional power/steam plants. The SO₂ concentration in the refinery exhaust is reduced by 80 %, but CO₂ emissions increase.

The use of by-product and residual streams to meet the fuel requirement of refineries is not only cost-effective, but is also environmentally beneficial, in that it makes use of what would otherwise be a waste refinery stream that would be flared without recovering the energy content.

Cross-media effects

In some cases, some difficulties may occur in burning low-calorific-value gas produced. Water effluent is normally sent to the existing waste water treatment plant of the refinery. It may contain significant amounts of metals such as V, Cr or Ni and PAH.

Operational data

Utility requirements for the gasification processes are 1 800 – 4 900 kWh/t of power and 1 140 kg/t of steam consumption. The soot product is about 50 – 75 % w/w V₂O₅ residue, which can be sold to metal reclaimers. The IGCC complex is also equipped with all the necessary auxiliary systems, including cooling water (mixed system with an open seawater circuit for

large users and a closed clean water circuit for the other users), demi-water, air, nitrogen, water and fuel gas networks, firefighting, flare, storage, electrical distribution, buildings, etc.

IGCC is a technology with high flexibility in start-up, shutdown and part-load operation, depending on the level of integration between the different sections. Typically, systems that use heat exchange equipment are more efficient than those using quench cooling; however, the capital cost of the system with heat exchange is higher and there is a risk of fouling. The handling of the soot and filter cake should be done with care to avoid dust (even at 80 % moisture), due to the toxic properties of the residue.

Applicability

This technique can be seen as an alternative approach to removing sulphur-using feed hydrotreatment (see Section 4.10.2.3). During normal refinery operation, the gasifiers of the IGCC plant are able to convert almost any refinery residue (atmospheric residues, vacuum residues, visbroken or thermal tars, etc.) to heat and power. These feedstocks can have a high sulphur content.

Economics

Table 4.44 gives the economics of two examples of IGCC applied in European refineries.

Table 4.44: Economics of two IGCC plants in European refineries

| Refinery capacity | | Mt/yr |
|--|--|---------------------|
| Fuel used in the refinery | 120 000 liquid 180 000 gaseous | t/yr |
| Volume of flue-gas generated in the refinery | 1.68×10^9 | Nm ³ /yr |
| SO _x emissions (as SO ₂) before application of IGCC | 5 000 (for liquid refinery fuels with 3 % S) | mg/Nm ³ |
| SO _x emission load | 8 400 | t/yr |
| Efficiency of the process measured as sulphur content of the gaseous fuel | 0.01 | % |
| Investment cost | 200 – 400 | EUR million |
| Operating costs | 20 – 40 | EUR million/yr |

| Size of the IGCC | 280 | MW |
|---------------------------------------|------------------------------|--------------------|
| Net cogeneration efficiency | 47.2 | % |
| Investment cost | 648 | EUR million |
| Characteristics of the feedstock used | Density: 1.05 – 1.1 | kg/dm ³ |
| | Viscosity: 100 – 3 500 | cts at 150 °C |
| | Sulphur: 3.5 – 7 | % |
| | Metals: 300 – 800 | ppm |
| | Heating value: 8 800 – 9 200 | kcal/kg |

Example plant(s)

The IGCC concept as such is quite a recent technological application for power stations. Although the main sections of an IGCC plant, i.e. gasification, air separation, gas cleaning and combined cycle, are well-known techniques that have previously been used separately for different applications and with different feedstocks. Integration (the 'I' in IGCC), though, is a more recent idea. Oil gasification is a process that has been applied for many years. Gasification of heavy residues, according to the principles of IGCC, is rather new. At least four IGCC plants are already in operation within European refineries and some others are in the design/construction phase. Coal gasification, also applying the IGCC concept, is new as well and a few plants are in operation.

Reference literature

[151, Sema, Sofres 1991], [221, Italy 2000], [232, Italy 1996].

4.10.3.5 Fluidised bed boiler

Description

An alternative method for the use of heavy residual oils or petroleum coke is combustion in a fluidised boiler with limestone injection for sulphur capture.

Achieved environmental benefits

About 90 % of the sulphur content of the fuel is captured and about 50 % of the calcium in the limestone is used in sulphur absorption.

Cross-media effects

The resulting calcium sulphate and unconverted calcium oxide, together with the nickel and vanadium in the fuel, are discharged from the boiler as a solid residue, which can be used as road aggregate or disposed of to landfill.

However, such schemes have a lower sulphur capture performance than gasification and they do not provide the option of producing hydrogen. There could also be environmental objections to the mining and transport of limestone and disposal of the residue. For these reasons, gasification may be generally more attractive in the long term.

Applicability

A combination of fluidised bed boilers with upstream solvent deasphalting or delayed coking can be a cost-effective solution for refineries with existing FCC unit capacity and steam/power deficiencies.

Economics

Typically cheaper than gasification.

Driving force for implementation

Reduction of solid waste generation.

Reference literature

[168, VROM 1999].

4.10.4 Nitrogen oxide control and abatement techniques

Techniques to reduce NO_x emissions fall into two broad categories. Primary techniques that include NO_x control techniques, such as precombustion operational changes and combustion modifications. Secondary techniques that include the post-combustion flue-gas treatments or NO_x abatement techniques. More information about NO_x abatement techniques can be found in Section 4.23.3. Primary and secondary techniques are considered in this section. The types of NO_x control and abatement techniques to be considered in the energy systems are summarised in Table 4.45.

Table 4.45: NO_x control and abatement techniques considered for energy systems

| Type of techniques | Fired heaters | Boilers | Gas turbines |
|---|---|---|--|
| Primary measures (control techniques) | Low-NO _x burners Ultra-low-NO _x burners Reburning | Flue-gas recirculation Ultra-low-NO _x burners Low-NO _x burners Reburning | Dry low-NO _x combustors Steam injection Water injection Low-NO _x combustors |
| Secondary measures (abatement techniques) | SCR SNCR | SCR SNCR | SCR |

4.10.4.1 Low-NO_x burners and ultra-low-NO_x burners

Description

Low-NO_x burners, either air-staged or fuel-staged, have the aim of reducing peak temperatures, reducing the oxygen concentration in the primary combustion zone, and reducing the residence time at high temperatures, thereby decreasing thermally formed NO_x. Moreover, in the case of fuel-staged burners, the understoichiometric conditions created by the secondary flame after the complementary addition of fuel creates a further chemical reduction of NO_x in N₂ by NH₃, HCN and CO radicals.

Ultra-low-NO_x burners add the internal or external recirculation of flue-gases to the basic low-NO_x burner design, enabling the decrease of the oxygen concentration in the combustion area and a further abatement of NO_x, acting in particular on fuel-burn. Further information on various burner designs and features can be found in Section 3.4.1.6 of the BREF on Large Combustion Plants [7, COM 2006].

Achieved environmental benefits

When successfully implemented, low-NO_x burners can achieve NO_x reduction performances of 40 – 60 % for gaseous fuels and 30 – 50 % for liquid fuels compared to conventional burners of the same thermal capacity. Respectively, ultra-low-NO_x burners successfully applied to gas-fired process heaters and boilers can achieve a 60 – 75 % reduction of NO_x emissions.

Based on the TWG 2008 data collection questionnaires (see Table 4.46), the following ranges have been reported from operational data at some EU-27+ refineries:

- 65 – 150 mg/Nm³ for gas-fired in all cases, except for one old retrofit where a value of 253 mg/Nm³ was observed;
- 190 – 470 mg/Nm³ for mixed gas liquid-fired (upper end reported for 50 % liquid firing).

The replacement of old burners with new low-NO_x burners, along with the air/fuel control system, may also have a positive effect on:

- process energy efficiency, as new burners are generally more fuel-efficient;
- noise generated by the combustion plant, as a global improvement opportunity.

Cross-media effects

For heavy liquid fuel firing, there is a direct link between NO_x and particulates, i.e. reduction in NO_x as the flame temperature falls will lead to an increase in particulates. CO emissions are also increased.

Operational data

Table 4.46 and Figure 4.38 give a selection of results reported by various European refineries within the data collection process launched for the BREF review (TWG 2008).

Table 4.46: Reported performance of low-NO_x burners in TWG site-level questionnaires

| Reference [Questionnaire] | Type of fuel/burner | Emissions (daily average) mg/Nm ³ at 3 % O ₂ | Available comments |
|---------------------------|---------------------|--|---|
| [no 1] | Gas-fired LNB | <100 | Process furnaces using generally RFG or NG Values <150 for steam cracker |
| [no 13] | Gas-fired LNB | 123 | 6 staged fuel burners - retrofit (2008) HDS unit – abatement achieved: 60 % |
| [no 14] | Gas-fired LNB | 253 142 97 | Retrofit (1991 – 2000) Retrofit (2006) Retrofit (2006) |
| | Mixed-fired LNB | 297 191 315 | Retrofit (1991 – 2000) 110 LNB out of 128 222 LNB out of 242 |
| [no 16] | Gas-fired LNB | 104 (monthly) | Max. (spot): 194 |
| | Mixed-fired LNB | 317 (monthly) | Max. (spot): 400 |
| [no 20] | Gas-fired LNB | 100 | Average ranges achieved on 2 RFG-fired and 1 mixed-fired furnaces equipped with first generation LNB |
| | Mixed-fired LNB | 300 | |
| [no 22] | Gas-fired LNB | 80 – 120 | Average ranges achieved on a large number of furnaces equipped with LNB |
| | Mixed-fired LNB | 200 – 250 | |
| [no 26] | Gas-fired LNB | 65 | 6 staged fuel burners - retrofit (2002) on a 20 MW furnace |
| [no 37] | Mixed-fired LNB | 301 317 330 – 360 336 469 322 | 30/70 fuel to gas 34/66 fuel to gas 40/60 fuel to gas 45/55 50/50 58/42 (N content in liquid fuel: 0.6 %) |
| [no 38] | Mixed-fired LNB | 435 | 50/50 fuel to gas N content: 2.44 % (liquid)/0.47 % (solid) H ₂ in fuel gas: 32 % (mass) |
| [no 39] | Gas-fired LNB | 54 | Concentration calculated from 15 mg/MJ Vacuum heaters - retrofit (1991) Achieved abatement: 80 % |
| | Gas-fired LNB | 72 | Concentration calculated from 20 mg/MJ Crude heaters - retrofit (1998) Achieved abatement: 65 % |
| [no 46] | Gas-fired LNB | <125 | LNB burners Last generation of burners: 2 000 |
| | Liquid-fired LNB | <250 | Achievable with low throughput and low oxygen demand |
| [no 47] | Gas-fired LNB | 93 | Achieved with ULSG burners |
| | Mixed-fired LNB | 340 | Best boiler - 50/50 fuel to gas |
| | Mixed-fired LNB | 220 | Best furnace - 50/50 fuel to gas |

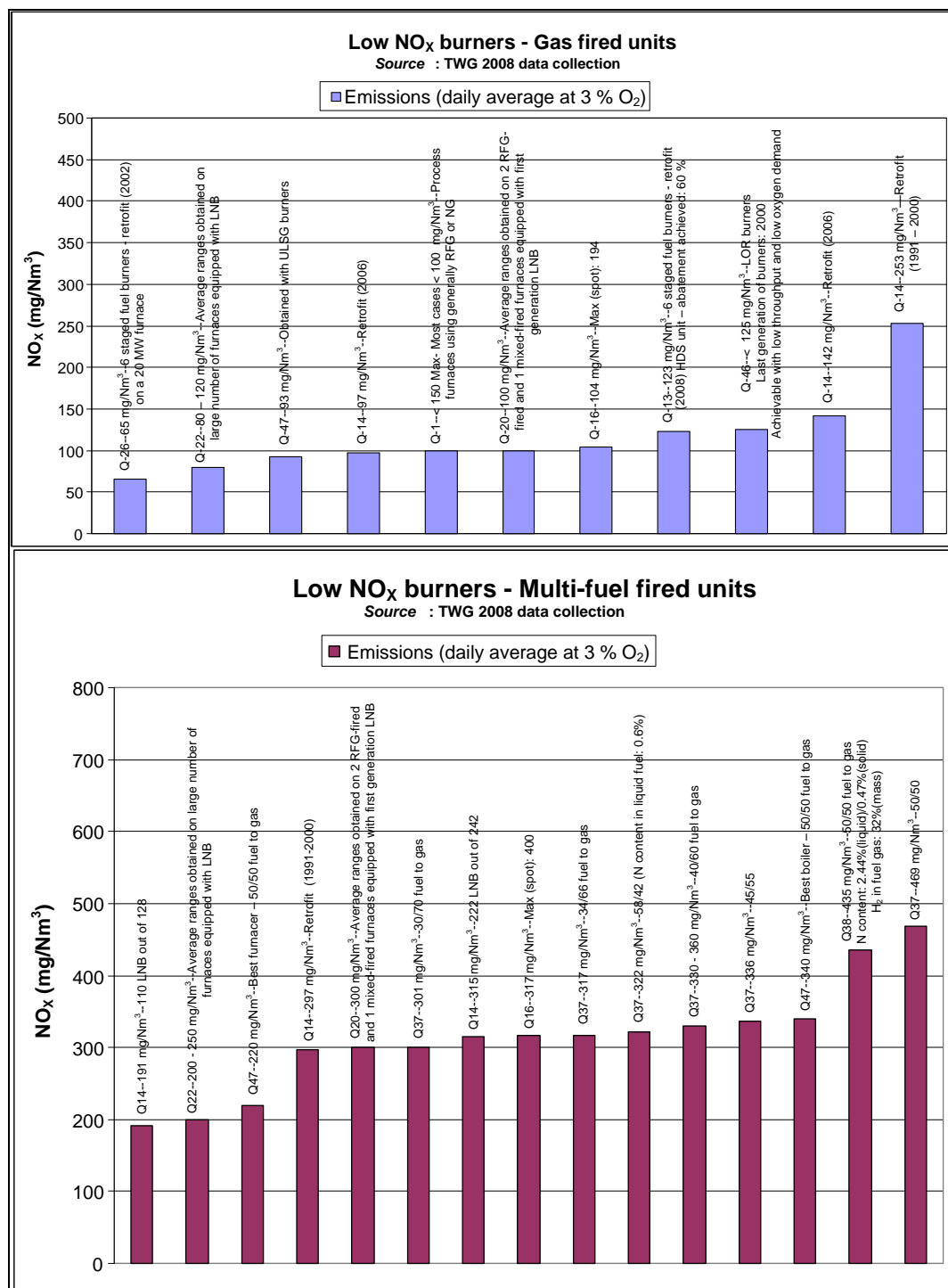


Figure 4.38: Reported performance of low-NO_x burners for gas-fired and multi-fuel-fired combustion units (data from Table 4.46)

Extensive work has been undertaken to develop correlations that help explain how NO_x emissions relate to changes in operational parameters, e.g. fuel type and composition (in particular fuel-bound nitrogen), combustion air preheat temperature, and firebox temperature. A good example is given by the set of adjustment factors developed in the Netherlands and provided as a national guidance for permit writers in 1987 [36, CONCAWE 4/09 2009 (Appendix I)].

Table 4.47 shows a summary of typical ranges of NO_x emissions achieved in real refining operating conditions. These ranges cover a spectrum of different situations resulting from these

variable conditions, and are considered for air combustion converted back to ambient air temperature.

Table 4.47: Typical ranges of emissions measured under various refining operating conditions in retrofit situations

| Fuel | Type of burner | Emissions (daily average) | Comments |
|-------------------|---|--------------------------------|--|
| Refinery fuel gas | Low-NO _x burner with air or fuel basic staging | 80 – 140 ⁽¹⁾ | For combustion air at ambient temperature |
| | Ultra-low-NO _x burner First generation | 60 – 90 ⁽¹⁾ | For combustion air at ambient temperature |
| | Ultra-low-NO _x burner Latest generation | 30 – 60 ⁽¹⁾⁽²⁾ | For combustion air at ambient temperature and firebox temperature <900° |
| Mixed gas/liquid | Dual-fired Low-NO _x burner (fuel staging for gas only) | 200 – 350 ⁽¹⁾⁽²⁾⁽³⁾ | For combustion air at ambient temperature. Lowest values achieved for 25 – 50 % liquid firing (0.21 – 0.5 % N content). Highest values achieved with 50 – 70 % liquid firing (0.4 – 0.55 % N content). |

(¹) Lower values are achievable with a firebox temperature of <800 °C and <10 % v/v of hydrogen or C3 + in the refinery fuel gas composition.
(²) Lower values are achievable with fuel gas containing no ammonia or other fuel-bound nitrogen.
(³) Lower values are achievable with <0.1 % fuel-bound nitrogen mass content in the liquid fuel burnt.
NB: Units in mg/Nm³ at 3 % O₂.
Source: [36, CONCAWE 4/09 2009]

For the gas refining sector in Norway, the following table shows recent examples of the use of ultra-low-NO_x burners.

Table 4.48: Recent example of ultra-low-NO_x burners in natural gas plants in Norway

| Site | Thermal input capacity | Type of burner/fuel/year | NO _x emissions | Comments |
|-------------|------------------------|--|--------------------------------------|---|
| Ormen Lange | 2 x 42.1 MW | Ultra-low-NO _x burner with flue-gas recirculation/ Natural gas/2007 | 20 mg/Nm ³ | Measurements in 2008 in the range of 20 – 90 mg/Nm ³ (30 – 10 MW) – NO _x emissions vary <i>inversely</i> to the MW of heat applied to the ovens |
| Kollsnes | 18.4 MW | Ultra-low-NO _x burner/ Natural gas/2012 ⁽²⁾ | 30 mg/Nm ³ ⁽¹⁾ | |

(¹) Value guaranteed by supplier for 60 – 100 % operating duty range of the heater.
(²) Heater planned to be in operation in 2012 and used instead of existing one.
NB: Units in mg/Nm³ at 3 % O₂.

Applicability

New installations

Apart from fuel-specific limiting conditions (see below), application is straightforward for new heaters and boilers.

Retrofitting existing installations

Compared to conventional burners, usual low- and ultra-low-NO_x burners of the same thermal capacity tend to stretch the flame length up to 50 % and the flame diameter up to 30 – 50 %. They also need more space (internal and external area and volume) for being installed as their

footprint is also increased, due to the presence of fuel injectors and/or the incorporation of furnace gas recirculation devices in and outside the burner tile. Finally, they usually offer a lower flexibility ('turndown' capability ratio) between the highest and lowest accessible firing rates for given operating conditions, raising operating constraints and potential safety concerns.

Therefore, some older fired heaters are fitted with large high-intensity burners which cannot be easily retrofitted with new low-NO_x burners. As an illustration of this, some cases of disappointing results have been reported within the data collection process for the review of this BREF. Another example is the retrofitting of dual-fuel burners theoretically capable of operating with 100 % gas fuel, but with a practical restriction on the maximum amount of gas due to tube skin temperature limits in the primary and secondary super-heater section [Questionnaires n° 31, 32, 37, 45].

The retrofitting of low-NO_x burners is possible in general but will depend on site-specific conditions (such as furnace design and surrounding environment). Nevertheless, in some specific cases, it can lead to heavily modifying the technical integration of the furnace into the unit, or to changing the furnace.

Some state-of-the-art burners have been specifically designed for being retrofitted to existing plants, and may be very well adapted to the upgrading of oil refining gas-fuelled heaters. They benefit from advanced computational fluid dynamics (CFD) modelling and show a higher compactness associated with an improved turndown capability.

Fuel-specific limiting conditions

The applicability for state-of-the-art gas-fired ultra-low-NO_x burners is limited to fuel gases having a small amount of components heavier than propane and a low olefinic content. NO_x performance with ultra-low-NO_x burners (ULNB) is more sensitive to excess oxygen. Therefore, this performance will depend on the feasibility and reliability of oxygen concentration control in the firebox (see Section 4.10.3.1 and Figure 4.35).

Economics

The following table gives different cost examples for the installation of low-NO_x burners, derived from various retrofitting projects in refineries.

Table 4.49: Specific cost examples for the retrofitting of low- and ultra-low-NO_x burners

| Project/reference | Investment cost | Comments |
|---|---|---|
| 1/Reburning a typical crude oil furnace consisting of 40 forced-draught burners <i>No reference</i> | GBP 2 million (1998) Average per individual burner: GPD 50 000 | Including the general upgrading of the furnace air, fuel and control systems likely to be carried out at the same time by a refiner |
| 2/Retrofit several plants with gas-fired low-NO _x burners as follows: - vacuum heaters - crude heaters [Site questionnaire n°39] | Total investments: - SEK 11 million (1991) - SEK 41 million (1998) | Assuming a 5-year operation life: - 25 000 SEK/t per yr (80 t/yr NO _x saved) - 34 000 SEK/t per yr (220 t/yr NO _x saved) |
| 3a/Retrofit several process heaters operated within: - a CDU (10 Mt/yr – 20 burners) - a thermal cracker (3Mt/yr – 120 burners) - a HDS unit (12 burners) with: - gas-fired low-NO _x burners - ultra-low-NO _x burners [Site questionnaire n°42] | Pre-evaluation step: average for the overall + project involving 152 burners (early 2007) Cost per individual burner: - GBP 16 200 - GBP 17 200 | Does not include the general upgrading of the air, fuel and control systems. For the CDU unit: assumes a 5-year operation life: - GBP 639/t per yr (141 t/yr NO _x saved) - GBP 472/t per yr (202 t/yr NO _x saved) |
| 3b/Retrofit several process heaters operated in units including finally: - a CDU (10 Mt/yr – 20 burners) - an alkylation unit (0.4 Mt/yr – 6 burners) - a VDU (7 Mt/yr – 16 + 13 burners) - HDS units (12 + 12 burners) with: - ultra-low-NO _x burners [Site questionnaire No 42] | Updated evaluation step from 2A above (preliminary design): average for the overall final project involving 79 burners (early 2009) Cost per individual burner: - GBP 40 000 | Include the general upgrading of the air, fuel and control systems For the CDU unit: assuming a 5-year operation life: - GBP 644/t. y (202 t/yr NO _x saved) |
| 4/Retrofit 20 low-NO _x burners on a visbreaker furnace in 2008 [Site questionnaire No 13] | Total burners alone cost: EUR 140 000 (EUR 7 000/burner) Total installation cost: EUR 756 000 | Additional cost for burners' installation: + EUR 37 800/burner on average (+ 540 % of burner individual cost) |

The comparison between examples 2 and 3 in the table shows very clearly that given the small cost difference, an ultra-low-NO_x burner can be an excellent cost-effective option when it is possible to retrofit on a high-power installation, compared to low-NO_x burners.

Potential investment and operational costs, expressed as total annual costs, for implementing this technique in 2007 on RFG- and natural gas-fired process heaters in the Colorado refineries (US) were estimated as follows:

- For low-NO_x burners: EUR 2 818 (USD 3 817) per year and tonne of NO_x avoided, assuming a resulting NO_x emission decrease of 28 – 50 %;
- For ultra-low-NO_x burners (first generation): EUR 4 087 (USD 5 536 - based on currency conversion rate of 0.73822 on 1/07/2007) per year and tonne of NO_x avoided, assuming a resulting NO_x emission decrease of 55 %;
- For ultra-low-NO_x burners (last generation): EUR 613 – 908 (USD 831 – 1 230) per year and tonne of NO_x, avoided, assuming a resulting NO_x emission decrease of 75 – 85 %.

Driving force for implementation

Reduction of NO_x emissions, in combination with good cost-benefit conditions.

Example plants

There are many examples of applications in European refineries. At Preem Lysekil (SE), low-NO_x burners are used in 16 of 21 furnaces and boilers. At the Shell Gothenburg (SE) refinery, 85 % of the furnaces are equipped with low-NO_x burners.

Reference literature

[17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009].

4.10.4.2 Dry low-NO_x combustors**Description**

More information can be found in the LCP BREF [7, COM 2006].

Achieved environmental benefits

A 90 % reduction in NO_x emissions in natural gas-fired gas turbine applications is possible.

The main suppliers provide gas turbines equipped with dry low-NO_x combustors with a guarantee (for natural gas) of NO_x emissions of ≤ 9 to 40 ppmv (18 – 80 mg/Nm³) at 15 % O₂ dry conditions.

Table 4.50: NO_x emissions achieved with dry low-NO_x combustors for different types of equipment

| Type of fuel | Fired heaters | Boilers | Gas turbines |
|---|---------------|---------|--------------|
| Refinery fuel gas or natural gas | NA | NA | 20 – 90(*) |
| NB: Data in mg/Nm ³ at 15 % O ₂ . (g/GJ). NA: not applicable. (*) Where DLN are applicable. Source: [7, COM 2006], [264, G. Electric 2012], [265, Siemens 2012] | | | |

Cross media effects

None in particular.

Operational data

Dry combustors differ from burners as their performance increases with higher loads.

Applicability

Applicable to gas turbines. Dry low-NO_x combustors are not available for gas turbines fired with refinery blend gas that contains more than 5 – 10 % v/v of hydrogen. When using a high hydrogen content RFG in gas turbines, additional techniques such as diluent injection may be needed. [264, G. Electric 2012]

Economics

The investments costs are EUR 2.2 million (1998), and the operating cost is nil for an 85 MW_e output turbine.

Driving force for implementation

Reduction of NO_x emissions.

Reference literature

[166, CONCAWE 1999], [228, TWG 2000], [264, G. Electric 2012], [265, Siemens 2012]

4.10.4.3 Flue-gas recirculation

Description

External flue-gas recirculation (FGR) is applied to boilers and heaters to increase the diluent effect, hence to reduce the combustion temperature. Typically 20 % of the available flue-gas from the boiler stack is ducted to mix with fresh combustion air.

Achieved environmental benefits

Using recirculated flue-gas as part of the combustion air can further reduce NO_x formation.

Operational data

The process is difficult to control, especially during turndown.

Applicability

It is applied to boilers and fired heaters. In a retrofit (in particular boilers and furnaces in forced draught mode operation), FGR increases hydraulic loads, and shifts the heat load towards the convective section(s) and may not be practical.

Economics

Higher cost than other primary measures.

Driving force for implementation

To reduce the NO_x emissions from boilers and heaters.

Reference literature

[166, CONCAWE 1999], [228, TWG 2000].

4.10.4.4 Diluent injection

Description

Inert diluents, such as flue-gas, steam, water and nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NO_x in the flue-gases.

Achieved environmental benefits

Control of NO_x in gas turbine combustors may be carried out by using steam/water injection, which can achieve reduction performances of 80 – 90 %. Detailed data of NO_x emissions to air from gas turbines are shown in Table 4.43. Based on these data from continuous monitoring of a sample of gas turbines operated at some European refineries, the corresponding achievable range when using diluent injection is reported in Table 4.51.

Table 4.51: NO_x emissions achieved by gas turbines with diluent injection

| Type of fuel | NO _x emissions from gas turbines |
|---|---|
| Refinery fuel gas | 40 – 120 |
| NB: Data in mg/Nm ³ at 15 % O ₂ . | |
| Source: [145, TWG CONCAWE 2012] | |

Cross-media effects

When extra energy is required to produce steam, it could result in higher emissions and reduction of the overall system efficiency. An example of the energy debit of increasing steam addition to significantly reduce NO_x concentrations is reported for a 109 MW unit: a steam consumption of 13.7 t/h requires 11 MW of fuel to produce it (at 3 GJ fuel per tonne of steam).

Operational data

The use of steam generates more corrosion in the system than the use of nitrogen.

The data from continuous monitoring of a sample of gas turbines operated on a variable mix of refinery fuel gas at some European sites and using steam injection, show an operational range of 40 – 120 mg/Nm³ at 15 % O₂. See Table 4.43.

Applicability

Steam and water injection is widely applied to gas turbines both in new installations and retrofits and is also applicable to fired heaters and boilers. There are technical difficulties in applying water injection in boilers and furnaces. Nitrogen dilution is only applied when nitrogen is already available in the refinery.

Economics

Capital costs of the steam and water injection are less than those of SCR, making the technology a good first choice for substantial levels of NO_x reduction, with SCR often added on if higher NO_x reduction is needed. Substantial recurring operating costs are, however, encountered for producing high-purity steam, and maintenance costs for reblading may be high.

Driving force for implementation

Reduction of NO_x emissions.

Example plants

The nitrogen by-product from the air separation plant in refinery residue gasification projects has recently been proven commercially as a diluent for gas turbine NO_x reduction. Within the refining industry, steam injection predominates.

Reference literature

[145, TWG CONCAWE 2012], [163, FWE 1999], [166, CONCAWE 1999], [207, TWG 2001].

4.10.4.5 Fuel staging (reburning)

Description

Fuel staging, also called reburning, is based on the creation of different zones in the furnace by the staged injection of fuel and air. The aim is to reduce NO_x emissions, which have already been formed, back into nitrogen. This technique adds to the flame cooling, a reaction by which organic radicals assist in the breakdown of NO_x. More information is available in the LCP BREF [7, COM 2006].

Achieved environmental benefits

Achievable levels are <200 mg/Nm³ NO₂ equivalent, especially for gas firing, for which the lowest levels are more easily achievable.

Cross-media effects

Additional energy consumption (estimated at around 15 %, without any complementary energy recovery).

Applicability

This technique is applied at the furnace or boiler level but it is strongly connected with the burner technique. It is widely used for gas firing. For mixed or liquid firing, a specific burner design is required.

Driving force for implementation

Reduction of NO_x emissions.

Reference literature

[163, FWE 1999].

4.10.4.6 Selective non-catalytic reduction (SNCR)

Description

See Section 4.23.3.2 below.

Achieved environmental benefits

In oil refining, reductions of NO_x from 25 % to 70 % have been demonstrated under favourable conditions for full-size combustion plants.

Cross-media effects

General cross-media effects are described in Section 4.23.3.2 below.

In the particular context of oil refining, the effects given below are to be noted.

- A side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphate deposits give rise to the fouling and corrosion of cooler downstream equipment. Ammonium sulphate can also result in aerosol emissions from the stack and can contribute to PM emissions.
- The storage and use of gaseous or liquefied anhydrous ammonia has a great hazardous potential. If such storage is impossible to avoid, a risk assessment should be carried out and appropriate prevention measures are required. When technically possible, a liquid solution of ammonia (25 %) should always be preferred. Flue-gas temperature drops after urea or ammonia injection, which penalise the energy recovery potential.

Operational data

Table 4.52 gives some illustrative examples of this, for three boilers operated in oil refineries.

Table 4.52: NO_x emissions achieved with retrofitted SNCR for different refinery boilers

| Reference [Questionnaire] | Thermal capacity | Fuel type | % N in liquid fuel | % liquid fuel/total | Inlet concentration | % NO _x abatement | Comments |
|------------------------------|------------------|-----------|--------------------|---------------------|---------------------|-----------------------------|---|
| [no 13] | 98 MW | Mixed | 0.40 – 0.50 | 30 – 95 | 244 – 810 | 25 – 40 | 40 % only achieved for specific boiler load |
| [no 15] | 45 MW | Mixed | 0.34 – 0.45 | 80 – 95 | 667 – 877 | 25 – 30 | Ammonia slip >15 ppm for >30 % abatement |
| [no 15] | 45 MW | Mixed | 0.34 – 0.45 | 70 – 90 | 568 – 780 | 25 – 30 | |

NB: Emissions in mg/Nm³ at 3 % O₂ (dry gas). Continuous emission monitoring system for reference [no 13].
Source: [36, CONCAWE 4/09 2009]

These figures are consistent with an urea test performed from 2008 to 2009 in a French refinery on a 99 MW boiler. In the 104 t/h flue-gas stream, containing 600 – 800 mg/Nm³ (3 % O₂ dry) of NO_x, the initial urea injection rate was 150 – 200 l/h, corresponding to approximately 1 kg urea per kg NO_x to be treated. The NO_x reduction achieved was 35 – 45 %, with concentrations in the range of 380 – 400 mg/Nm³. However, after some tube perforations due to corrosion, the injection rate was reduced and then stopped for the injection conditions to be modified and optimised.

At the Gothenburg ST1 refinery (SE), it is reported that a SNCR unit operating at one boiler (45 MW) achieves the following reductions:

- from 300 to 150 mg/Nm³ for gas firing;
- from 1 100 to 550 mg/Nm³ for oil firing.

Applicability

SNCR requires temperatures within the following window:

- 850 – 1 000 °C, for ammonia and caustic ammonia (optimum 870 °C);
- 800 – 1 100 °C, for urea (optimum 1 000 °C).

Retrofitting to existing boilers and furnaces can be limited, as there may not be sufficient residence time (0.2 – 0.5 s in the region of injection) at the required temperature levels.

Thus, application of the SNCR technique in existing furnaces and boilers requires well chosen injection locations and a mixing region with an appropriate temperature and size to allow for sufficient NO reduction.

Application is also complicated when the flue-gases to be treated come from the combustion of high sulphur content heavy fuel oil for which ammonia slips can lead to the formation of ammonium sulphate deposits.

When retrofitting, new space requirements may be very limited, especially ammonia storage and injection equipment.

Economics

Table 4.53 shows the economics of the application of SNCR for the treatment of flue-gases coming from the combustion processes from different sources. Cost data for SCR and SNCR used at combustion units for different sizes and abatement efficiencies are shown in Table 4.55.

Table 4.53: Examples and main cost factors for Selective Non-Catalytic Reduction (SNCR)

| Values corresponding to a 100 GJ/h installation - retrofit of existing installation | Fired heaters and boilers firing refinery blend gas | Boilers firing residual fuel oil |
|---|---|----------------------------------|
| Down to ppm at 3 % O ₂ | 50 | 100 |
| Investment costs (1998) (EUR million) | 0.4 – 0.5 | 0.4 – 0.9 |
| Operating costs per year (excludes capital charge) (EUR million) | 0.025 | 0.05 – 0.07 |

| | | |
|---|--|---------------------|
| Capacity of the refinery | 5 | Mt/yr |
| Fuel consumption | 120 000 (liquid refinery fuels) 180 000 (refinery fuel gas) | t/yr |
| Volume of the flue-gas | 3 10 ⁹ | Nm ³ /yr |
| Efficiency of the SNCR | 60 – 80 | % |
| NO _x emissions (as NO ₂) | 200 | mg/Nm ³ |
| Investment | 3 – 5 | EUR million |
| Operating costs | 0.2 – 1 | EUR million/yr |

| Cost parameters | | EUR/unit | EUR/yr |
|---|-----------|----------|---------|
| Operating hours (h/yr) | 8 000 | | |
| Investment (EUR) | 1 090 093 | | |
| Input factors for annual expenditure: | | | |
| Number of years | 15 | | |
| Interest rate (%) | 6 | | |
| Annual repayment incl. interest (EUR/yr) | 112 239 | | |
| Proportional investment incl. interest | | | 112 239 |
| Maintenance + wear and tear (% of investment costs) | 2 | | |
| Maintenance + wear and tear (EUR/yr) | 21 802 | | |
| Maintenance + wear and tear | | | 21 802 |

| Cost parameters | | EUR/unit | EUR/yr |
|--|-------|--------------------------|----------------|
| Electrical energy (kWh/h) | 40 | 0.07 EUR/kWh | 20 930 |
| Air (Nm ³ /h) | 1 200 | 0.01 EUR/Nm ³ | 118 602 |
| NH ₃ liquid (kg/h) | 83.15 | 0.25 EUR/kg | 169 201 |
| Total cost | | | 442 774 |
| NB: Installation on a volume of exhaust gas of 250 000 Nm ³ /h after a power plant, in a refinery achieving a NO _x emission reduction of 500 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <200 mg NO _x /Nm ³ . | | | |

Potential investment and operational costs for implementing this technique in 2007 on process heaters in the Colorado refineries (US) were estimated at EUR 3 644 (USD 4 936 - based on currency conversion rate of 0.738 22 on 1/07/2007) per year and tonne of NO_x avoided, assuming a resulting NO_x emission decrease of 43 – 60 %. Another set of data gathered during an applicability test on a French refinery site (see details under operational data) gave less expensive costs, as shown in Table 4.54 below.

Table 4.54: Cost evaluation for urea SNCR retrofitting of a 99 MW refinery boiler (2009)

| Urea SNCR retrofitting costs to a 99 MW boiler | Costs (EUR) | Comments |
|--|--|--|
| Investment cost | 500 000 | Project year 2009 |
| Operational costs: | 539 000 | (Excluding capital charges) |
| Including: | | |
| Urea 200 l/h | 376 000 | EUR 190/t – 1980 t/yr |
| Equipment rental | 100 000 | |
| Energy for vaporisation (40 % urea in water) | 55 000 | 180 kW estimated |
| maintenance | 8 000 | 120 hours |
| Inlet concentration: 700 mg/Nm ³ Outlet concentration: 420 mg/Nm ³ Reduction 40 % NO _x : 330 t/yr | | 37.7 kg/h (Excluding capital charges) |
| Specific cost for 2009 | EUR/t of NO _x 1 935 | |

Table 4.55: Cost data for combustion unit NO_x abatement techniques (SCR and SNCR)

| NO _x Abatement on Combustion Units (Assuming SNCR Efficiency of 30%) | | | | | | | | | | | | | | | |
|---|------------|-----------------------|-----------------------|-------------------------------------|--------------------------------|-------------------------------|------------------------|-------------------------------------|--------------------------------|------------------------------|---------------------------------|---|--------------------|----------------------------------|---|
| Baseline | | | | SNCR | | | | | SCR | | | | | | |
| | | | | Efficiency | ACC | Fixed OP | Variable OP (50MW) | | Efficiency | ACC | Fixed OP | Variable OP (50MW) | | Cost-Effectiveness: Base to SNCR | Incremental Cost-Effectiveness: SNCR to SCR |
| | | | | % | % | %/y | k€/y | | % | % | %/y | k€/y | | | |
| Heat Fired | Oil | Stack NO _x | Stack NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SNCR | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SCR | Cost-Effectiveness: Base to SCR | Incremental Cost-Effectiveness: SNCR to SCR | | | |
| MW | % Total MW | mg/Nm ³ | mg/Nm ³ | t/y | M€ | k€/y | €/tNO _x | mg/Nm ³ | t/y | M€ | k€/y | €/tNO _x | €/tNO _x | | |
| Unit 1 | 289 | 72% | 450 | 315 | 328 | 2.9 | 730 | 2 225 | 70 | 924 | 18.3 | 2 445 | 2 645 | 2 876 | |
| Unit 2 | 179 | 75% | 450 | 315 | 204 | 2.2 | 496 | 2 434 | 70 | 574 | 13.7 | 1 788 | 3 117 | 3 492 | |
| Unit 3 | 123 | 31% | 356 | 250 | 111 | 1.7 | 368 | 3 318 | 55 | 312 | 10.9 | 1 401 | 4 491 | 5 136 | |
| Unit 4 | 254 | 30% | 351 | 245 | 225 | 2.7 | 657 | 2 923 | 54 | 634 | 16.9 | 2 247 | 3 546 | 3 889 | |
| Unit 5 | 76 | 45% | 425 | 298 | 81 | 1.3 | 251 | 3 099 | 66 | 229 | 8.2 | 1 025 | 4 483 | 5 245 | |
| Unit 6 | 51 | 77% | 450 | 315 | 58 | 1.0 | 187 | 3 218 | 70 | 163 | 6.5 | 799 | 4 890 | 5 811 | |
| Unit 7 | 158 | 21% | 305 | 213 | 122 | 2.0 | 448 | 3 684 | 47 | 343 | 12.7 | 1 649 | 4 807 | 5 425 | |
| Unit 8 | 89 | 10% | 250 | 175 | 56 | 1.4 | 285 | 5 075 | 39 | 158 | 9.0 | 1 138 | 7 185 | 8 346 | |
| Unit 9 | 215 | 5% | 227 | 159 | 123 | 2.4 | 573 | 4 658 | 35 | 346 | 15.3 | 2 010 | 5 804 | 6 434 | |
| Unit 10 | 170 | 0% | 200 | 140 | 86 | 2.1 | 475 | 5 533 | 31 | 242 | 13.3 | 1 728 | 7 142 | 8 028 | |
| Unit 11 | 63 | 0% | 200 | 140 | 32 | 1.2 | 219 | 6 873 | 31 | 90 | 7.3 | 915 | 10 173 | 11 989 | |
| Unit 12 | 46 | 0% | 200 | 140 | 23 | 0.9 | 172 | 7 438 | 31 | 65 | 6.0 | 746 | 11 453 | 13 662 | |
| NO _x Abatement on Combustion Units (Assuming SNCR Efficiency of 40%) | | | | | | | | | | | | | | | |
| Baseline | | | | SNCR | | | | | SCR | | | | | | |
| | | | | Efficiency | ACC | Fixed OP | Variable OP (50MW) | | Efficiency | ACC | Fixed OP | Variable OP (50MW) | | Cost-Effectiveness: Base to SNCR | Incremental Cost-Effectiveness: SNCR to SCR |
| | | | | % | % | %/y | k€/y | | % | % | %/y | k€/y | | | |
| Heat Fired | Oil | Stack NO _x | Stack NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SNCR | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SCR | Cost-Effectiveness: Base to SCR | Incremental Cost-Effectiveness: SNCR to SCR | | | |
| MW | % Total MW | mg/Nm ³ | mg/Nm ³ | t/y | M€ | k€/y | €/tNO _x | mg/Nm ³ | t/y | M€ | k€/y | €/tNO _x | €/tNO _x | | |
| Unit 1 | 289 | 72% | 450 | 270 | 437 | 2.9 | 730 | 1 669 | 70 | 924 | 18.3 | 2 445 | 2 645 | 3 522 | |
| Unit 2 | 179 | 75% | 450 | 270 | 272 | 2.2 | 496 | 1 825 | 70 | 574 | 13.7 | 1 788 | 3 117 | 4 277 | |
| Unit 3 | 123 | 31% | 356 | 214 | 148 | 1.7 | 368 | 2 488 | 55 | 312 | 10.9 | 1 401 | 4 491 | 6 289 | |
| Unit 4 | 254 | 30% | 351 | 210 | 300 | 2.7 | 657 | 2 192 | 54 | 634 | 16.9 | 2 247 | 3 546 | 4 762 | |
| Unit 5 | 76 | 45% | 425 | 255 | 108 | 1.3 | 251 | 2 324 | 66 | 229 | 8.2 | 1 025 | 4 483 | 6 423 | |
| Unit 6 | 51 | 77% | 450 | 270 | 77 | 1.0 | 187 | 2 413 | 70 | 163 | 6.5 | 799 | 4 890 | 7 116 | |
| Unit 7 | 158 | 21% | 305 | 183 | 162 | 2.0 | 448 | 2 763 | 47 | 343 | 12.7 | 1 649 | 4 807 | 6 643 | |
| Unit 8 | 89 | 10% | 250 | 150 | 75 | 1.4 | 285 | 3 806 | 39 | 158 | 9.0 | 1 138 | 7 185 | 10 220 | |
| Unit 9 | 215 | 5% | 227 | 136 | 164 | 2.4 | 573 | 3 494 | 35 | 346 | 15.3 | 2 010 | 5 804 | 7 879 | |
| Unit 10 | 170 | 0% | 200 | 120 | 115 | 2.1 | 475 | 4 150 | 31 | 242 | 13.3 | 1 728 | 7 142 | 9 830 | |
| Unit 11 | 63 | 0% | 200 | 120 | 43 | 1.2 | 219 | 5 155 | 31 | 90 | 7.3 | 915 | 10 173 | 14 682 | |
| Unit 12 | 46 | 0% | 200 | 120 | 31 | 0.9 | 172 | 5 579 | 31 | 65 | 6.0 | 746 | 11 453 | 16 730 | |
| NO _x Abatement on Combustion Units (Assuming SNCR Efficiency of 50%) | | | | | | | | | | | | | | | |
| Baseline | | | | SNCR | | | | | SCR | | | | | | |
| | | | | Efficiency | ACC | Fixed OP | Variable OP (50MW) | | Efficiency | ACC | Fixed OP | Variable OP (50MW) | | Cost-Effectiveness: Base to SNCR | Incremental Cost-Effectiveness: SNCR to SCR |
| | | | | % | % | %/y | k€/y | | % | % | %/y | k€/y | | | |
| Heat Fired | Oil | Stack NO _x | Stack NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SNCR | Outlet NO _x | NO _x Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to SCR | Cost-Effectiveness: Base to SCR | Incremental Cost-Effectiveness: SNCR to SCR | | | |
| MW | % Total MW | mg/Nm ³ | mg/Nm ³ | t/y | M€ | k€/y | €/tNO _x | mg/Nm ³ | t/y | M€ | k€/y | €/tNO _x | €/tNO _x | | |
| Unit 1 | 289 | 72% | 450 | 225 | 547 | 2.9 | 730 | 1 335 | 70 | 924 | 18.3 | 2 445 | 2 645 | 4 542 | |
| Unit 2 | 179 | 75% | 450 | 225 | 339 | 2.2 | 496 | 1 460 | 70 | 574 | 13.7 | 1 788 | 3 117 | 5 516 | |
| Unit 3 | 123 | 31% | 356 | 178 | 185 | 1.7 | 368 | 1 991 | 55 | 312 | 10.9 | 1 401 | 4 491 | 8 111 | |
| Unit 4 | 254 | 30% | 351 | 175 | 375 | 2.7 | 657 | 1 754 | 54 | 634 | 16.9 | 2 247 | 3 546 | 6 142 | |
| Unit 5 | 76 | 45% | 425 | 213 | 135 | 1.3 | 251 | 1 859 | 66 | 229 | 8.2 | 1 025 | 4 483 | 8 283 | |
| Unit 6 | 51 | 77% | 450 | 225 | 97 | 1.0 | 187 | 1 931 | 70 | 163 | 6.5 | 799 | 4 890 | 9 177 | |
| Unit 7 | 158 | 21% | 305 | 152 | 203 | 2.0 | 448 | 2 210 | 47 | 343 | 12.7 | 1 649 | 4 807 | 8 567 | |
| Unit 8 | 89 | 10% | 250 | 125 | 94 | 1.4 | 285 | 3 045 | 39 | 158 | 9.0 | 1 138 | 7 185 | 13 180 | |
| Unit 9 | 215 | 5% | 227 | 114 | 205 | 2.4 | 573 | 2 795 | 35 | 346 | 15.3 | 2 010 | 5 804 | 10 161 | |
| Unit 10 | 170 | 0% | 200 | 100 | 143 | 2.1 | 475 | 3 320 | 31 | 242 | 13.3 | 1 728 | 7 142 | 12 678 | |
| Unit 11 | 63 | 0% | 200 | 100 | 53 | 1.2 | 219 | 4 124 | 31 | 90 | 7.3 | 915 | 10 173 | 18 934 | |
| Unit 12 | 46 | 0% | 200 | 100 | 39 | 0.9 | 172 | 4 463 | 31 | 65 | 6.0 | 746 | 11 453 | 21 576 | |

Source: [139, CONCAWE 6/11 2011]

Driving force for implementation

Reduction of NO_x emissions.

Example plants

This process has been applied to heaters and boilers of refinery plants. Experience of application of SNCR on oil-fired heaters is more limited. A US study reports that SNCR is used less frequently than SCR for the control of NO_x and that only 12 of the 150 boilers/heater installations of eight refineries use this type of technique. In the EU, for example, Shell refinery in Gothenburg (SE) operates an SNCR on one boiler.

Reference literature

[17, Jeavons & Francis 2008], [36, CONCAWE n°4/09 2009], [151, Sema, Sofres 1991], [160, Janson 1999], [166, CONCAWE 1999], [194, Winter 2000], [246, AL Group 2001], [Questionnaire n° 13].

4.10.4.7 Selective catalytic reduction (SCR)**Description**

See Section 4.23.3.3 below.

Achieved environmental benefits

SCR is capable of reducing NO_x by 80 – 95 % in refining boilers and heater applications, as well as for gas turbine flue-gases.

Cross-media effects

Generic cross-media effects are described in Section 4.23.3.3.

In the particular context of oil refining, the effects given below are to be noted.

- As for the SNCR technique, a side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphate deposits give rise to the fouling and corrosion of cooler downstream equipment. Ammonium sulphate can also result in aerosol emissions from the stack and contribute to PM emissions.
- As for the SNCR technique, the storage and use of gaseous or liquefied anhydrous ammonia has a great hazardous potential. If such storage is impossible to avoid, a risk assessment should be carried out and appropriate prevention measures taken. When technically possible, a liquid solution of ammonia (25 %) is preferred.

Operational data

At a Shell refinery (SE), a SCR unit has been installed at a 68 MW boiler (1998). Fuel oil is used and NO_x emissions are 16 mg/MJ (55 mg/Nm³, 3 % O₂). The NO_x reduction is about 94 % and the ammonia slip well below 5 ppm. Preem Lysekil (SE) has a SCR unit on the FCC (see Section 4.5.4.1). Preem refinery Gothenburg (SE) has two SCR units, on the reformer and one on one of the two crude distillation units.

At the STEAG power station (TOTAL Mitteldeutschland refinery in Germany), the three oil-fired heaters (each producing 160 t/h steam -100 bars - 505 °C, consuming 12 t/h of heavy fuel oil at 3.7 % S) are equipped with a SCR plant (high-dust); they have to reach NO_x emissions below 150 mg/m³. Table 4.56 below gives more data concerning this particular example.

Table 4.56: Gas concentration of the power plant of the TOTAL Mitteldeutschland refinery

| Parameters (yearly average 2009) | Raw gas | Clean gas |
|---|---------|-----------|
| Flue-gas volume, wet (m ³ /h, 7 % O ₂) | 171 690 | 188 249 |
| Temperature (°C) | <180 | <76 |
| Dust (mg/Nm ³ , 3 % O ₂) | 220 | <10 |
| NO _x as NO ₂ (mg/Nm ³ , 3 % O ₂) | 800 | <150 |
| SO ₂ (mg/Nm ³ , 3 % O ₂) | <4 100 | |
| SO ₃ (mg/Nm ³ , 3 % O ₂) | 650 | <10 |
| SO _x as SO ₂ (mg/Nm ³ , 3 % O ₂) | | <220 |

Moreover, CONCAWE reports two other data-sets of SCR in refineries, one covering a mixed gas/oil-fired heater, and the other covering a common stack of four mixed gas/oil-fired boilers. In both cases, an 80–82 % removal is shown, resulting in a 90–120 mg/Nm³ outlet concentration (3 % O₂).

Finally, one recent example of SCR has been reported for a 19 MW refinery gas turbine application in France. After the operation restarted in 2009, early results showed an 80 % NO_x decrease from concentrations registered before (maximum 350 mg/Nm³) to new maximum concentrations measured below 65 mg/Nm³ (15 % O₂). A 2 % loss of the generated power was reported.

Applicability

Section 4.23.3.3 below gives general considerations on the usual constraints for the retrofitting of the SCR technique to existing combustion plants, notably in terms of space availability, temperature and pressure drop.

In the particular case of boilers and heaters of refineries fired with heavy fuels, fly ash contains metal oxides, soot and coke. Unabated fly ash concentrations are in the range of 100–600 mg/Nm³ (with the highest values corresponding to vacuum residues). SCR applied under these conditions may suffer from clogging by fly ash and sulphates. The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5–4 %).

NO_x removal efficiency will also depend on the NO_x inlet concentration to be abated because, even under optimal thermal conditions, there is a lower limit to the technically achievable reduction yield and outlet concentration, due to the particular mixing conditions and chemical kinetics.

Economics

The costs of SCR vary, depending on the fuels, exhaust volume and required NO_x reduction.

For new power generation installations, the cost range may be EUR 25–110/kW. Maintenance costs are minimal, the bulk of which are from NH₃ consumption.

For retrofitting situations, two examples of the application of SCR in refinery power plants are shown in Table 4.57 and Table 4.58. The use of a SCR unit for treating the power plant flue-gas has been estimated in raw gas (Table 4.58) and clean gas (Table 4.57) operation mode. These two cost tables refer to the TOTAL Mitteldeutschland refinery project in the two cases already mentioned, for which performance data are provided in Table 4.56.

Table 4.57: Main cost factors for Selective Catalytic Reduction (SCR) in clean gas operation

| Cost details (clean gas operation) in 1998 | Quantity | EUR/unit | EUR/yr |
|--|-----------|---------------------------|------------------|
| Operating hours (h/yr) | 8 000 | | |
| Investment (EUR) | 3 270 278 | | |
| Input factors for annual expenditure: | | | |
| Number of years | 15 | | |
| Interest rate (%) | 6 | | |
| Annual repayment incl. interest (EUR/yr) | 336 717 | | |
| Proportional investment costs incl. interest | | | 336 717 |
| Volume of catalyst (m ³) | 20 | | |
| Endurance (years) | 15 | | |
| Renewal of catalyst (m ³ /yr) | 1.33 | 14 535 EUR/m ³ | |
| Average renewal of catalyst (EUR/yr) | 19 379 | | |
| Catalysts | | | 19 379 |
| Maintenance + wear and tear (% of investment costs) | 2 | | |
| Maintenance + wear and tear (EUR/yr) | 65 406 | | |
| Maintenance + wear and tear | | | 65 406 |
| Pressure drop (mbar) | 35 | | |
| Energy for reheating (MJ/h) | 11 806.67 | 3.63 EUR/GJ | 343 210 |
| Electrical energy (kWh/h) | 610 | 0.07 EUR/kWh | 319 187 |
| NH ₃ liquid (kg/h) | 46.20 | 0.25 EUR/kg | 94 001 |
| Total costs (1998) | | | 1 177 900 |
| NB: Installation on a volume of exhaust gas of 250 000 Nm ³ /h in the dedusted off-gas after a power plant, in a refinery achieving a NO _x emission reduction of 500 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <100 mg NO _x /Nm ³ . | | | |

Table 4.58: Main cost factors for Selective Catalytic Reduction (SCR) in raw gas operation

| Cost details (raw gas operation) in 1998 | Quantity | EUR/unit | EUR/yr |
|--|-----------|---------------------------|----------------|
| Operating hours (h/yr) | 8 000 | | |
| Investment costs (EUR) | 2 180 185 | | |
| Input factors for annual expenditure: | | | |
| Number of years | 15 | | |
| Interest rate (%) | 6 | | |
| Annual repayment incl. interest (EUR/yr) | 224 478 | | |
| Proportional investment costs incl. interest | | | 224 478 |
| Volume of catalyst (m ³) | 35 | | |
| Endurance (years) | 8 | | |
| Renewal of catalyst (m ³ /yr) | 4.38 | 14 535 EUR/m ³ | |
| Average of catalyst (EUR/yr) | 63 589 | | |
| Catalysts | | | 63 589 |
| Maintenance + wear and tear (% of investment costs) | 2 | | |
| Maintenance + wear and tear (EUR/yr) | 43 604 | | |
| Maintenance + wear and tear | | | 43 604 |
| Pressure drop (mbar) | 8 | | |
| Energy for reheating (MJ/h) | 0 | 3.63 EUR/GJ | 0 |
| Electrical energy (kWh/h) | 160.07 | 0.07 EUR/kWh | 83 753 |
| NH ₃ liquid (kg/h) | 46.20 | 0.25 EUR/kg | 94 001 |
| Total costs (1998) | | | 509 425 |
| NB: Installation (raw gas) on a volume of exhaust gas of 250 000 Nm ³ /h after a power plant, in a refinery achieving a NO _x emission reduction of 500 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <100 mg NO _x /Nm ³ . | | | |

Table 4.59 illustrates another retrofitting cost example, for the reformer furnace of the Swedish Preem refinery, also in 1998.

Table 4.59: Investment costs for retrofitting SCR to a reformer furnace (1998)

| | Data | Comments |
|---------------------------------|-----------------|--|
| Capacity | 68 MW | Total reformer thermal capacity |
| Efficiency (design) | 90 % | Designed for low temperature: 185 °C Ammonia slip of 5 ppm |
| Efficiency (operational) | 91 % | Achieved value until 2009 In 2009: 75 % including one month out of operation for revision |
| Investment cost (1998) | EUR 3.2 million | |

Cost data for SCR and SNCR used at combustion units for different sizes and abatement efficiencies are shown in Table 4.55.

Moreover, potential investment and operational costs for implementing this technique in 2007 on existing boilers and process heaters in Colorado refineries (US) were estimated at a range of EUR 2 000 to 6 054 (USD 2 708 to USD 8 201) per year and tonne of NO_x avoided, assuming a resulting NO_x emission reduction of 70 – 90 % (based on currency conversion rate of 0.738 22 on 1/07/2007).

For retrofitting a 19 MW refinery gas turbine in France, the following costs were reported:

- total construction cost (2008): EUR 7 million;
- annual cost: EUR 200 000.

Driving force for implementation

Reduction of NO_x emissions.

Example plant(s)

Concerning refinery energy systems, SCR has been applied to gas turbines, process boilers, process heaters such as naphtha reformers, steam reformers, crude and vacuum distillation units, thermal cracking and hydroprocessing units. A report on US refineries shows that 20.7 % (or 31 boilers/heaters) of 150 boiler/heater installations at eight refineries employ SCR as a control technique. The same study shows that three SCR installations have been applied to the four turbines found in the eight refineries analysed.

Reference literature

[17, Jeavons & Francis 2008], [36, CONCAWE 4/09 2009], [151, Sema, Sofres 1991], [160, Janson 1999], [166, CONCAWE 1999], [183, HP 1998], [194, Winter 2000], [246, AL Group 2001], [Questionnaire n° 9].

4.10.4.8 Low-temperature oxidation

Description

See Section 4.23.3.1.

Achieved environmental benefits

Reduction of NO_x emission by 90 – 95 %, with an outlet concentration reduced to 10 ppm.

See Section 4.23.3.1.

Cross-media effects

Low-temperature oxidation (LoTO_x) should be necessarily associated with a new or existing scrubbing unit, which generates waste water to be treated properly. An increase in nitrate load to the existing WWTP might have to be considered, together with the associated cost to control nitrates. Nitric acid is produced and needs to be neutralised with an alkali used in the scrubbing section.

In order to oxidise the NO_x to soluble higher oxides, ozone is required and should be generated on site using an ozone generator, which consumes oxygen and electrical energy.

Operational data

NO_x removal performance is directly linked to the ozone injection rate. It can be regulated on a real-time basis in relation to the NO_x outlet concentration target. The outlet NO_x can be adjusted by varying the set point on the system controller. Reported values show that the control level was set up in order to respect the permit conditions of 20 ppm.

Applicability

The LoTO_x process operates optimally above 150 °C and does not require heat input to maintain operational efficiency, enabling maximum heat recovery from the flue-gas. Applicable to both new and retrofitted applications.

In the case of retrofitting, a separate tower may have to be built in order to provide the required additional ozone injection and reaction stage. Ozone slip out of the stack will be associated with this technology. Appropriate design for additional processes related to ozone generation and personnel safety have to be taken into account.

The applicability may be limited by the need for additional waste water treatment. It should also be taken into consideration that an appropriate supply of liquid oxygen for ozone generation is needed. The applicability of the technique may also require significant space availability.

Economics

No data available.

Driving force for implementation

Demands for very low NO_x emissions in the case of installations either already equipped with a wet scrubbing system or aimed at being treated with such.

Example plants

There have been examples of applications since 1997 in the US for two small gas-fired boilers (California) and one coal-fired 25 MW power plant (Ohio).

Reference literature

[18, [Confuorto 2007](#)].

4.10.4.9 Catalytic reduction of CO and NO_x**Description**

The technology uses a single platinum-based catalyst coated with potassium carbonate (K₂CO₃) that operates in two cycles: oxidation/absorption and regeneration. The catalyst works by simultaneously oxidising CO to CO₂ and NO to NO₂, and then absorbing NO₂ onto its surface through the use of a potassium carbonate absorber coating. The regeneration of the catalyst is accomplished by passing a controlled mixture of regeneration gases across the surface of the catalyst in the absence of oxygen. The regeneration gases are steam, hydrogen and carbon dioxide. Consequently the nitrates are reduced to nitrogen. An additional catalyst layer is required to reduce SO₂ emissions and preserve the CO- and NO_x-reducing catalyst when sulphur is present in the fuel.

Because the regeneration cycle should take place in an oxygen-free environment, a section of catalyst undergoing regeneration must be isolated from exhaust gases. This is accomplished using a set of louvers, one upstream of the section being regenerated and one downstream. During the regeneration cycle, these louvers close and a valve opens, allowing regeneration gas into the section.

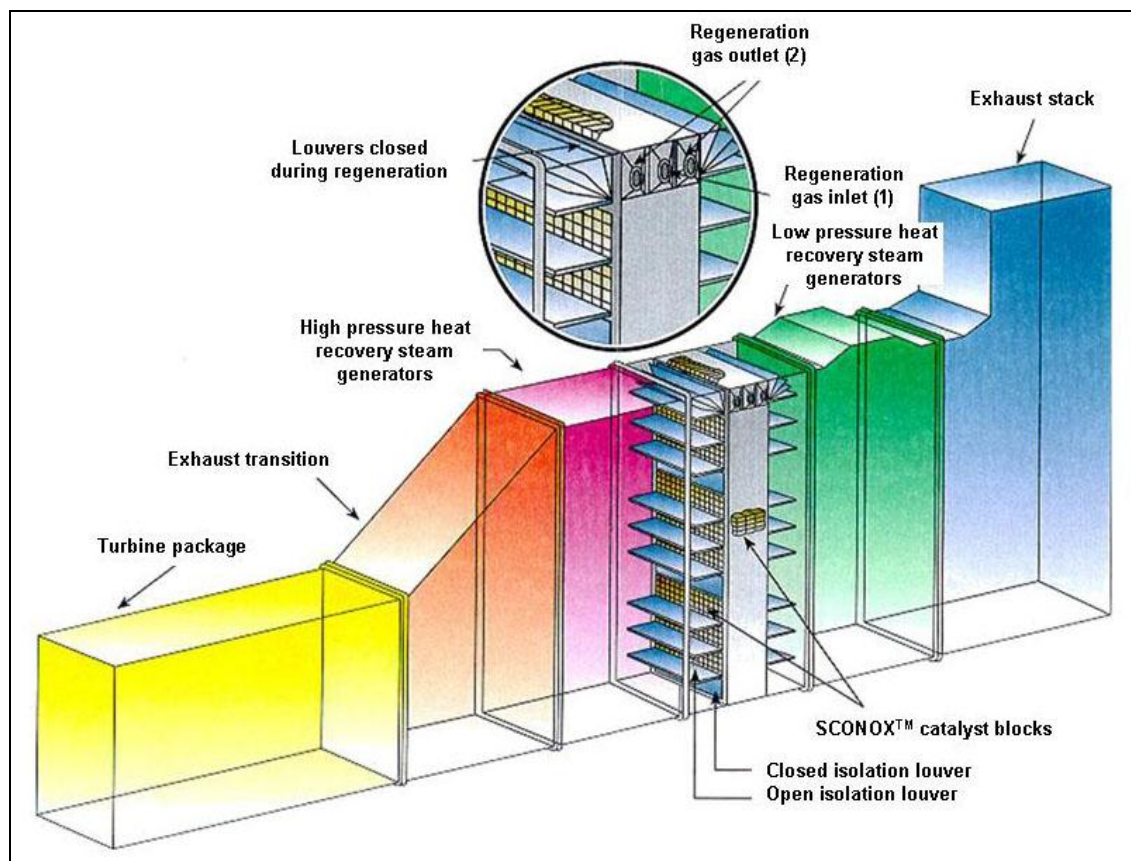


Figure 4.39: Schematic presentation of the catalyst system

Achieved environmental benefits

By using this technique, combined cycle turbines can be operated with very low NO_x emission levels. At the same time, the system reduces emissions of CO and non-methane volatile organic compounds. It uses no ammonia. In conjunction with a sulphur-removal catalyst technique this system can also be used for reducing sulphur compounds from exhaust gas if required. Achievable levels are the following:

- NO_x emissions below 2 ppm (4 mg/Nm³ as NO_2 at standard conditions 0 °C; 1 013 mbar);
- conversion rate of CO into CO_2 is 90 %;
- destruction of non-methane volatile organic compounds (NMVOC) greater than 90 % at 315 °C;
- destruction of formaldehyde and acetaldehyde, measured at 97 % and 94 % respectively at 150 °C.

Cross-media effects

The catalyst is very susceptible to fouling by sulphur in the flue-gas and may need an additional specific sulphur absorption catalyst. The system emits CO_2 , H_2O , N_2 and trace levels of SO_2 to the stack. Due to the masking and poisoning of the catalyst, annual or six-monthly catalyst cleaning is required with de-ionised water and a potassium carbonate solution (K_2CO_3). The spent cleaning fluids can be neutralised and disposed of through the sewerage system and are

harmless to the water and soil. Precious metals on the spent catalyst have a residual value and can be reclaimed. There is no waste disposal issue caused by spent catalyst.

Operational data

This system requires electricity for control systems, valves and actuators, natural gas for regeneration gas production and steam both for regeneration gas production and as a dilution carrier. The typical pressure drop is between 8.5 mbar and 15 mbar. The system can operate effectively at temperatures ranging from 150 °C to 370 °C. The utility requirements for a 25 MW gas turbine are steam (333 – 389 °C): 1 590 kg/h and natural gas: 14 kg/h.

The US EPA has stated its concerns (19 November 1999 letter) over the technical uncertainties of such a technique, especially about applying it to large combined cycle turbines.

Applicability

Applicable to both new and retrofitted applications, the system can operate effectively at temperatures ranging from 150 °C to 370 °C and does not limit gas turbine performance. Such a unit can be installed at the back of the boiler or in the heat recovery steam generator within the same envelope reserved for a conventional SCR system.

Economics

The estimated cost presented refers to a typical 400 MW size combined cycle gas-fired power plant. The cost estimate numbers below are based on 8 000 h/yr of operation and a NO_x reduction from 25 ppm to 5 ppm (50 to 10 mg/Nm³ as NO₂ at standard conditions 0 °C; 1 013 mbar), which equals approximately 666 tonnes annually of NO_x removed. Included in the numbers are investment costs, operational and maintenance costs and indirect annual costs.

| Cost | EUR million | Including |
|--|-------------|---|
| Investment | 19.2 | Delivery, erection and commissioning/start-up |
| Operation and maintenance | 1.6 | General maintenance; Steam and natural gas consumption in the regeneration cycle; Pressure drop across the unit (approx. 10 mbars) (converted to power consumption); Average cost/yr for catalyst replacement (7-year catalyst life for leading row); Catalyst disposal/refund. |
| NB: Additional indirect annual costs to the contractor are not included. | | |

A reduction of NO_x from 25 ppm to 2 ppm (50 to 4 mg/Nm³ as NO₂ at standard conditions 0 °C; 1 013 mbar) will contribute to an increase in the investment due to the need for additional catalyst. It will also somewhat increase the operation and maintenance costs due to the increased consumption of natural gas and steam and increased pressure drop.

A second example gives an installation cost of EUR 6.2 million for the application of this technique to a gas turbine of 25 MW. The operating costs are estimated to be approximately EUR 0.42 million/yr, including maintenance, steam and natural gas, pressure drop through the system, and the cost of catalyst replacement.

Driving force for implementation

Demands for very low NO_x emissions and limitations of air pollution control equipment utilising ammonia, especially for plants situated in densely populated areas.

Example plants

There are example applications in the US in small gas power plants. For example, a combustion turbine of 32 MW is operating at the Federal Cold Storage Cogeneration facility in California.

Reference literature

[91, JEA 2008], [207, TWG 2001], [211, Power 2000].

4.10.5 Particulate abatement techniques

Particulate loads (containing metals) from refinery combustion plants are normally fairly low, unless heavy residues are burnt. These particulates may be abated using a number of methods, including electrostatic precipitators (ESP), bag filters and wet scrubbing, as described in Section 4.23.4.

4.10.5.1 Switching to low-ash content fuels

Description

Refinery fuel gas and hydrotreated liquid refinery fuels contain lower particulate loads than heavy liquid refinery fuels. Switching to these fuels has a positive impact on the reduction of particulates emissions. The achieved emission particulate levels, as well as cross-media effects, operational data, applicability and economics have already been described in Sections 4.10.2 and 4.10.3.1).

4.10.5.2 Steam atomisation for liquid fuel

Description

Steam injection while burning the liquid refinery fuel leads to atomisation and to lowering the particulate concentration.

Achieved environmental benefits

In the flue-gas of the firing liquid refinery fuel of older furnaces, the PM content may range from 500 to 1 000 mg/Nm³. For new optimal burner designs with steam atomisation, this can be in the range of 20 – 250 mg/Nm³ (see Section 4.10.3.1). For boilers, all these figures are, on average, lower. The range of 150 – 500 mg/Nm³ represents the current typical range with liquid fuels employed (ash contents) and burners installed (low-NO_x with steam atomisation).

Cross-media effects

Improved fuel oil atomisation reduces the droplet size and leads to an increase in the intensity of combustion. This results in higher flame temperatures and can lead to increased NO_x emissions.

Applicability

Steam injection in fired furnaces/boilers is widely practised with liquid fuel.

Driving force for implementation

Reduction of particulate emissions.

Reference literature

[168, VROM 1999].

4.10.5.3 Electrostatic precipitator (ESP)

Description

For more information, see Section 4.23.4.2.

Achieved environmental benefits

ESPs can achieve particulate matter (PM) emissions of <10 – 50 mg/Nm³ with up to 95 % reduction. Soot blowing is an operation that is carried out at regular intervals to remove soot

that has accumulated on the furnace equipment and which has hampered proper functioning. During this operation, the PM content of the exhaust gas can reach values of 2 000 mg/Nm³. ESPs and similar dust removal techniques installed for normal operations are effective in reducing the PM emissions to the accepted level. Thus, ESPs working on process furnaces normally yield higher average concentrations due to soot blowing.

Cross-media effects

Electricity consumption, dust disposal and, in some cases, ammonia emissions. For more information see Section 4.23.4.

Operational data

More information in Section 4.23.4.

Applicability

ESPs are widely applied in FCC units, in thermal power plants and in incinerators. ESPs may not be applicable for some particulates with high electric resistance. They can be installed in both new and existing plants. They require space for their application.

Economics

Typical installed capital costs for ESPs are from EUR 1 million to 3.8 million.

Driving force for implementation

Reduce emissions of particulates and metals or other hazardous substances contained on them.

Examples

Wet ESPs are the most common type used for the abatement of particulates in heavy fuel oil combustion processes. In refineries, ESPs are used both in FCC units and in heavy oil and residue cracker units. They can be used to treat emissions from heavy liquid or solid fuel combustion.

Reference literature

[151, Sema, Sofres 1991], [191, UBA Austria 1998].

4.10.6 Sulphur oxides abatement techniques

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Techniques to reduce sulphur oxides emissions are fuel optimisation, fuel desulphurisation (hydrotreatments described in Section 4.10.2.3) or flue-gas desulphurisation. The lower the sulphur content of the fuel, the lower the emission of sulphur dioxide. In this section, techniques for the capture of SO₂ from the flue-gas after combustion or flue-gas desulphurisation techniques and the use of additives are included. More general information on these techniques is given in Section 4.23.5.4.

4.10.6.1 Additives to fuels

Description

- Technique 1: Use of lime or limestone as an additive to fuels to capture the sulphur oxides.
- Technique 2: Use of magnesium-based additives for the inhibition of the SO₂ to SO₃ oxidation. Magnesium combines with the vanadium pentoxide generated during the heavy liquid fuels' combustion.

Achieved environmental benefits

- Technique 1: This technique abates the SO₂ release by about 90 %. 100 % limestone in excess of the stoichiometric quantity is required.

- Technique 2: The purpose of this technique is not to reduce SO_x emissions, but to reduce the amount of SO₃ in the plume for mitigating its visibility.

Cross-media effects

- Technique 1: A limestone/gypsum mixture has to be disposed of.
- Technique 2: No noticeable effects to be mentioned.

Operational data

Technique 2: The injection rate used has been around one litre for every 5.6 tonnes of liquid fuel burnt.

Applicability

- Technique 1: For conventional refinery boilers and furnaces, the injection of lime or limestone into the furnace for sulphur capture cannot be applied. If the heaters and boilers are fluidised bed or circulating fluid boilers to burn petroleum coke or heavy bitumen resulting from solvent deasphalting, then lime/limestone injected into the furnace as abatement would be practical.
- Technique 2: This technique was applied as a trial (2008) in a European refinery to reduce the visible plume from two out of the six boilers. In 2010, the technique was out of service, as the site was not able to quantitatively prove the improvements achieved.

Driving force for implementation

Reduced sulphur oxide emissions.

Reference literature

[151, Sema, Sofres 1991], [Questionnaire No 45].

4.10.6.2 Flue-gas desulphurisation processes

Description

The techniques that may be considered for application to the flue-gas desulphurisation are for example wet limestone scrubber, the Walther process, the Wellman-Lord process, the SD process, the AI process, the SNO_x process and seawater scrubbing. Detailed information about these processes can be found in Section 4.23.5.4.

Economics

Recent cost data for the use of a wet gas scrubber compared to fuel substitution (natural gas replacing refinery fuel oil) are presented in Table 4.60 (data from [139, CONCAWE 6/11 2011]).

Table 4.60: Cost data for combustion unit SO₂ abatement techniques: comparison between wet gas scrubber and substitution of refinery fuel oil (RFO) by natural gas

| SO ₂ Abatement on Combustion Units (NG to RFO Spread at net 75€/tFOE) | | | | | | | | | | | | | | |
|---|------------|--|----------|-----------------------|-----------------------|-------------------------------------|--------------------------------|-----------------------------|----------------------------------|-----------------------|-------------------------------------|--------------------------------|------------------------------|---------------------------------|
| Baseline | | Substitution of Refinery Fuel Oil with Natural Gas | | | | | | | Installation of Wet Gas Scrubber | | | | Variable OP (50MW) | |
| | | | | | | | | | Efficiency | ACC | Fixed OP | | | |
| | | Net Cost of Natural Gas (Cost-Value of Displaced RFO €/tFOE) | | | | | | | 75 | % | % | %TEC/y | | k€/y |
| | | (Includes annualised cost of project to supply NG to Refinery) | | | | | | | | 90% | 7.4% | 4% | 433 | |
| | Heat Fired | Oil | S in Oil | Stack SO ₂ | Stack SO ₂ | SO ₂ Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to NG | Cost-Effectiveness: Base to NG | Stack SO ₂ | SO ₂ Removed (From Base) | Total Erected Cost (From Base) | Annualised Cost: Base to WGS | Cost-Effectiveness: Base to WGS |
| | MW | % Total MW | % | mg/Nm ³ | mg/Nm ³ | t/y | M€ | k€/y | €/tSO ₂ | mg/Nm ³ | t/y | M€ | k€/y | €/tSO ₂ |
| Unit 1 | 289 | 72% | 1.8% | 2 616 | 484 | 5 180 | NA | 12 091 | 2 334 | 262 | 5 721 | 34.4 | 6 422 | 1 123 |
| Unit 2 | 179 | 75% | 1.7% | 2 282 | 165 | 3 194 | NA | 7 812 | 2 446 | 228 | 3 098 | 25.8 | 4 497 | 1 452 |
| Unit 3 | 123 | 31% | 3.9% | 2 222 | 163 | 2 133 | NA | 2 251 | 1 056 | 222 | 2 072 | 20.6 | 3 416 | 1 649 |
| Unit 4 | 254 | 30% | 0.9% | 569 | 118 | 964 | NA | 4 473 | 4 642 | 57 | 1 095 | 31.8 | 5 832 | 5 326 |
| Unit 5 | 76 | 45% | 0.9% | 777 | 102 | 429 | NA | 1 991 | 4 642 | 78 | 444 | 15.4 | 2 408 | 5 418 |
| Unit 6 | 51 | 77% | 0.4% | 531 | 10 | 224 | NA | 2 284 | 10 212 | 53 | 205 | 12.2 | 1 828 | 8 901 |
| Unit 7 | 158 | 21% | 0.5% | 191 | 16 | 232 | NA | 1 938 | 8 337 | 19 | 228 | 24.0 | 4 103 | 17 961 |
| Unit 8 | 89 | 10% | 1.1% | 209 | 21 | 141 | NA | 522 | 3 714 | 21 | 141 | 17.0 | 2 705 | 19 179 |
| SO ₂ Abatement on Combustion Units (NG to RFO Spread at net 100€/tFOE) | | | | | | | | | | | | | | |
| | | Net Cost of Natural Gas (Cost-Value of Displaced RFO €/tFOE) | | | | | | | 100 | % | % | %TEC/y | k€/y | |
| | | (Includes annualised cost of project to supply NG to Refinery) | | | | | | | | 90% | 7.4% | 4% | 433 | |
| Unit 1 | 289 | 72% | 1.8% | 2 616 | 484 | 5 180 | NA | 16 121 | 3 112 | 262 | 5 721 | 34.4 | 6 422 | 1 123 |
| Unit 2 | 179 | 75% | 1.7% | 2 282 | 165 | 3 194 | NA | 10 416 | 3 261 | 228 | 3 098 | 25.8 | 4 497 | 1 452 |
| Unit 3 | 123 | 31% | 3.9% | 2 222 | 163 | 2 133 | NA | 3 002 | 1 407 | 222 | 2 072 | 20.6 | 3 416 | 1 649 |
| Unit 4 | 254 | 30% | 0.9% | 569 | 118 | 964 | NA | 5 964 | 6 189 | 57 | 1 095 | 31.8 | 5 832 | 5 326 |
| Unit 5 | 76 | 45% | 0.9% | 777 | 102 | 429 | NA | 2 654 | 6 189 | 78 | 444 | 15.4 | 2 408 | 5 418 |
| Unit 6 | 51 | 77% | 0.4% | 531 | 10 | 224 | NA | 3 045 | 13 617 | 53 | 205 | 12.2 | 1 828 | 8 901 |
| Unit 7 | 158 | 21% | 0.5% | 191 | 16 | 232 | NA | 2 584 | 11 116 | 19 | 228 | 24.0 | 4 103 | 17 961 |
| Unit 8 | 89 | 10% | 1.1% | 209 | 21 | 141 | NA | 696 | 4 951 | 21 | 141 | 17.0 | 2 705 | 19 179 |
| SO ₂ Abatement on Combustion Units (NG to RFO Spread at net 150€/tFOE) | | | | | | | | | | | | | | |
| | | Net Cost of Natural Gas (Cost-Value of Displaced RFO €/tFOE) | | | | | | | 150 | % | % | %TEC/y | k€/y | |
| | | (Includes annualised cost of project to supply NG to Refinery) | | | | | | | | 90% | 7.4% | 4% | 433 | |
| Unit 1 | 289 | 72% | 1.8% | 2 616 | 484 | 5 180 | NA | 24 181 | 4 669 | 262 | 5 721 | 34.4 | 6 422 | 1 123 |
| Unit 2 | 179 | 75% | 1.7% | 2 282 | 165 | 3 194 | NA | 15 624 | 4 892 | 228 | 3 098 | 25.8 | 4 497 | 1 452 |
| Unit 3 | 123 | 31% | 3.9% | 2 222 | 163 | 2 133 | NA | 4 503 | 2 111 | 222 | 2 072 | 20.6 | 3 416 | 1 649 |
| Unit 4 | 254 | 30% | 0.9% | 569 | 118 | 964 | NA | 8 946 | 9 284 | 57 | 1 095 | 31.8 | 5 832 | 5 326 |
| Unit 5 | 76 | 45% | 0.9% | 777 | 102 | 429 | NA | 3 981 | 9 284 | 78 | 444 | 15.4 | 2 408 | 5 418 |
| Unit 6 | 51 | 77% | 0.4% | 531 | 10 | 224 | NA | 4 568 | 20 425 | 53 | 205 | 12.2 | 1 828 | 8 901 |
| Unit 7 | 158 | 21% | 0.5% | 191 | 16 | 232 | NA | 3 875 | 16 673 | 19 | 228 | 24.0 | 4 103 | 17 961 |
| Unit 8 | 89 | 10% | 1.1% | 209 | 21 | 141 | NA | 1 044 | 7 427 | 21 | 141 | 17.0 | 2 705 | 19 179 |

Source: [139, CONCAWE 6/11 2011]

4.10.7 Combustion units abatement techniques' performance and emissions variability

Table 4.61 shows the achieved emissions values expressed as minimum and maximum monthly concentration (at 3 % O₂ level) observed from continuous monitoring for a number of refinery combustion units in Europe for SO₂, NO_x and dust and the determining operating conditions or the currently applied techniques at these units.

The data summarised in Table 4.61 are based on daily values from time series for periods from one to up to four years, generally including 2011. [145, TWG CONCAWE 2012]

From these data and the operating conditions and techniques in use, the main factors influencing the emissions to air of the combustion units are the following:

- For SO₂ emissions, the main driver is the fuel sulphur content: the sulphur (S) going into the combustion units is the result of the combination of:

- the sulphur content in oil (the fuel oil sulphur content can vary over time);
- the sulphur content in gas;
- the ratio of oil to gas.

- For NO_x emissions, several factors need to be considered:
 - the burner and furnace conditions (e.g. burner design, furnace rating, air preheat);
 - the firing duty (firing rate/design rate);
 - the fuel composition (e.g. H₂ content, heating value);
 - the fuel nitrogen (N) content for oil firing;
 - the abatement technique in place.

- Dust emissions are mainly affected by:
 - the type of fuel;
 - the burner and furnace conditions;
 - the firing duty.

In addition, a survey carried out in 2012 on a number of multi-firing combustion units (of more than 50 MW) currently operating at refineries in Italy confirms that the day-to-day variability of SO₂ and NO_x emissions is directly linked to the percentage of use of fuel oil to refinery fuel gas due to the adjustment of the refinery to the energy balance needs and to the sulphur content of the fuel oil.

According to this survey, the variability of the ratio of use of fuel oil/fuel gas changes from site to site and from plant to plant, consequently leading to a broad daily variability of the emissions to air of SO₂ and NO_x. [278, TWG-IT 2012]

Table 4.61: Emission data from a sample of combustion units at some European refineries

| Site and unit | Shared Stack | Rating, MW | Fuel | H ₂ content of RFG % v/v | Technique | NO _x | | SO ₂ | | Dust | | Comments |
|------------------|--------------|------------|------|-------------------------------------|-------------------|-----------------|--------------|-----------------|--------------|--------------|--------------|--|
| | | | | | | Min. monthly | Max. monthly | Min. monthly | Max. monthly | Min. monthly | Max. monthly | |
| Site J Furnace B | yes | 130 | Gas | 0 - 90 | Air-staged LNB | 200 | 250 | | | | | Variable fuel properties and firing duty. The furnace is connected to a common stack but has a separate analyser for NO _x . Variable operating conditions affect the NO _x concentration: <u>large variations</u> in duty firing (50 – 100 %) and in overall fuel gas composition: H ₂ content (0 – 90 % H ₂). |
| Site J Furnace A | | 160 | Gas | 5 - 26 | LNB | 80 | 90 | | | | | |
| Site J Furnace E | | 66 | Gas | 12 - 47 | LNB | 200 | 300 | | | | | NO _x changes with air-preheat temperature and load and with fuel hydrogen content. Fuel hydrogen changes not available. |
| Site J Furnace F | | 66 | Gas | 12 - 47 | LNB | 180 | 300 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace G | | 55 | Gas | 12 - 47 | LNB | 140 | 300 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace H | | 66 | Gas | 12 - 47 | LNB | 70 | 250 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace I | | 66 | Gas | 12 - 47 | LNB | 120 | 180 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace J | | 66 | Gas | 12 - 47 | LNB | 60 | 230 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace K | | 55 | Gas | 12 - 47 | LNB | 80 | 130 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace P | | 37 | Gas | 30-60 | LNB | 70 | 140 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace Q | | 40 | Gas | 30-60 | LNB | 140 | 180 | | | | | Idem previous comment - J Furnace E |
| Site J Furnace R | | 40 | Gas | 30-60 | LNB | 60 | 130 | | | | | Idem previous comment - J Furnace E |
| Site G | several | | Gas | | LNB, Conventional | 200 | 250 | | | | | Common stack shared by several furnaces. Refinery fuel gas being fired. |
| Site B Stack 1 | 8 furnaces | 296 | Gas | 20 - 45 | LNB and/or ULNB | 80 | 100 | | | | | The averaging effect of combining flue-gas from 8 furnaces may account for the low variability in the NO _x concentration. |

| Site and unit | Shared Stack | Rating, MW | Fuel | H ₂ content of RFG % v/v | Technique | NO _x | | SO ₂ | | Dust | | Comments |
|-----------------|--------------|------------|------|-------------------------------------|-----------------|-----------------|--------------|-----------------|--------------|--------------|--------------|--|
| | | | | | | Min. monthly | Max. monthly | Min. monthly | Max. monthly | Min. monthly | Max. monthly | |
| Site B Stack 3 | 5 furnaces | 86 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 180 | 220 | | | | | No information on the actual variation over the period. Suspect that fuel is reason for higher emissions in first half (averaging in stack would compensate individual furnace condition changes). |
| Site B Stack 2 | 5 furnaces | 90.2 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 230 | 290 | | | | | |
| Site B Stack 4 | 3 furnaces | 112 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 160 | 210 | | | | | Shared stack. 3 furnaces (20.8, 25.7 and 66 MW). Lower NO _x concentration found when the largest furnace is at low load. |
| Site B Stack 5 | 3 furnaces | 110 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 120 | 155 | | | | | |
| Site B Stack 6 | 1 | 6 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 90 | 175 | | | | | |
| Site B Stack 7 | 1 | 21.5 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 180 | 300 | | | | | |
| Site B Stack 8 | 1 | 10 | Gas | | LNB and/or ULNB | 135 | 230 | | | | | |
| Site B Stack 9 | | 24 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 180 | 335 | | | | | |
| Site B Stack 10 | | 18 | Gas | 22.5 - 50.5 | LNB and/or ULNB | 170 | 220 | | | | | |
| Site B Stack 11 | 1 | 16 | Gas | | LNB and/or ULNB | 230 | 305 | | | | | |
| Site B Stack 12 | 1 | 29 | Gas | | LNB and/or ULNB | 100 | 125 | | | | | |
| Site B Stack 13 | 1 | 106 | Gas | | LNB and/or ULNB | 190 | 235 | | | | | Oscillations at the beginning of the year unexplained by load, operating conditions or fuel quality. |
| Site V Unit 4 | | | Gas | | LNB | 40 | 70 | | | | | No information on load or operating conditions is available |
| Site V Unit 5 | | | Gas | | LNB | 50 | 90 | | | | | No information on load or operating conditions. Load is expected to be variable and includes an out-of-service interval. |
| Site V Unit 6 | | | Gas | | LNB | 105 | 145 | | | | | Unit operating on low load. |

| Site and unit | Shared Stack | Rating, MW | Fuel | H ₂ content of RFG % v/v | Technique | NO _x | | SO ₂ | | Dust | | Comments |
|---------------------|--------------|------------|---------------------------------------|-------------------------------------|------------------|-----------------|--------------|-----------------|--------------|--------------|--------------|---|
| | | | | | | Min. monthly | Max. monthly | Min. monthly | Max. monthly | Min. monthly | Max. monthly | |
| Site W Plant 5 | | | Gas | | LNB | 120 | 200 | | | | | Operating through the overall combustion plant shutdown so possibly supplying steam requirement |
| Site W Plant 6 | | | Gas | | LNB | 135 | 200 | | | | | |
| Site W Plant 7 | | | Gas | | LNB | 130 | 160 | | | | | |
| Site N | | 164 | RFO+VRO | | | 420 | 510 | | | | | NO _x trends follow changes in amount if oil firing. VRO is vacuum residue oil. |
| Site G | 4 | | VGO+RFG | | Standard burners | 250 | 370 | 120 | 650 | | | VGO is vacuum gas oil |
| Site AZ | 3 | 185 | 1 – 3 % S oil, 0.015 % S gas | | | | | 400 | 1 500 | | | Monitoring: Calculated from fuel S content |
| Site AY CDU furnace | 1 | 254 | oil 0.75 –3 % gas 0.03 % | | | | | 750 | 1 700 | | | Monitoring: Calculated from fuel S content |
| Site AY Boiler 7 | | | oil 0.75 –3 % gas 0.03 % | | | | | <100 | 1 500 | | | Monitoring: Calculation associated with measure of sulphur content of the fuel or CEM both systems |
| Site AY Boiler 5 | | 49 | oil 0.75 –3 % gas 0.03 % | | | | | <100 | 1 550 | | | Monitoring: Calculation associated with measure of sulphur content of the fuel or CEM both systems |
| Site AZ | | 200 | oil 0.75 –1 % gas 0.05 % | | | | | 600 | 1 000 | | | Monitoring: Calculation associated with measure of sulphur content of the fuels |
| Site N | | 164 | 25 – 50 % oil firing VRO+RFG | | | | | 900 | 1 250 | | | Fuel oil S content and amount of fuel oil fired determine the SO ₂ emission, |
| Site U Unit 1 | | 100 | 83 % oil-fired, 1.9 % S, 0.3 % N | | | 250 | 480 | 1 500 | 2 800 | 25 | 70 | <u>Suspect data error in June</u> as SO ₂ is high and NO _x is low at the same time. Dust concentrations are lower and less variable in second half of year. SO ₂ and NO _x are also lower: could reflect a difference in fuel mix or recalibration of opacity meter. |
| Site U Unit 2 | | 164 | Oil between 13 % and 35 % over period | | | 180 | 315 | 750 | 1 300 | 10 | 55 | August SO ₂ looks affected by zero data. Three periods of different oil/gas ratio are reflected in the SO ₂ , NO _x and Dust concentration time series |

| Site and unit | Shared Stack | Rating, MW | Fuel | H ₂ content of RFG % v/v | Technique | NO _x | | SO ₂ | | Dust | | Comments |
|---------------|--------------|------------|---|-------------------------------------|-----------|-----------------|--------------|-----------------|--------------|--------------|--------------|--|
| | | | | | | Min. monthly | Max. monthly | Min. monthly | Max. monthly | Min. monthly | Max. monthly | |
| Site U Unit 3 | | 280 | 61 % FO 1.9 % S 03 % N | | | 350 | 550 | 1 600 | 2 300 | 35 | 65 | Time series suggest changing fuel mix |
| Site V Unit 1 | | 34 | 19 % oil, RFO: 1.77 % w/w S | | | 47 | 325 | 177 | 1 210 | 25 | 48 | Corrected data (original monthly averages included missing data as zero concentration) |
| Site V Unit 2 | | 321 | Typical: 14 % fuel oil, 86 % gas. RFO: 1.77 % w/w S | | | 72 | 265 | 55 | 415 | 1 | 13 | Unit switched to gas part way through year. Corrected data (original monthly averages included missing data as zero concentration). Reported PM and SO ₂ values are very low after switch to gas firing, possibly this reflects problems in the analyser or calibration for high amounts of oil firing. |
| Site V Unit 3 | | 337 | 25 % RFO- 75 % RFG, RFO: 1.77 % w/w S | | | 150 | 360 | 450 | 1 100 | 2 | 45 | Time series suggest a switch to higher (or complete) switch to RFG firing after April (cf. V unit 2). |
| Site W Unit 1 | | | 60 % RFO | | LNB | 380 | 490 | - | - | - | - | |
| Site W Unit 2 | | | 33 % RFO | | | 280 | 360 | - | - | - | - | |
| Site W Unit 3 | | | 40 % RFO | | | 320 | 400 | 400 | 1 100 | 19 | 44 | SO ₂ time series added and monthly averages checked for influence of missing/zero values. |

Source: [145, TWG CONCAWE 2012]

4.11 Etherification

4.11.1 Catalytic distillation

Description

The catalytic distillation process combines reaction and fractionation into a single unit operation. It requires a two-reactor design, where one is a boiling-point fixed bed reactor, followed by final conversion in a catalytic distillation column. Reactors use an acidic ion exchange resin catalyst. For more information see Section 2.11.

Achieved environmental benefits

The increased conversion process efficiency decreases the energy consumption within the system per tonne of product manufactured.

Cross-media effects

This technique requires an additional reactor. Catalyst handling in elevated places during installation and catalysts change may cause safety risks.

Operational data

The advantages of the process where the reaction catalyst is within the distillation column include essentially complete iso-olefin conversions. Etherification can be applied for MTBE, ETBE or TAME production. Conversions of 98 % of isobutylene are typical for refinery feedstocks. Conversion is slightly less for ETBE than for MTBE. For TAME, isoamylene conversions of >95 % are achievable.

| Typical utility requirements, per m ³ of product | Range depending on the technology licensor | Units |
|---|--|----------------|
| Electricity | 1.3 – 3.1 | kWh |
| Steam (10.3 barg) | 600 – 1 150 | kg |
| Steam (3.4 barg) | 100 – 1 150 | kg |
| Water cooling ($\Delta T = 17$ °C) | 1.5 – 4 | m ³ |

Economics

Investment costs: EUR 18 850 per m³/d of MTBE product.

(Costs calculation based on 1999 rate EUR = 1.168 0 USD, for a 1 500 bpsd capacity unit and a cost of 3 500 USD per bpsd of MTBE.)

Example plants

This technique is widely applied.

Reference literature

[76, Hydrocarbon processing 2011], [183, HP 1998].

4.11.2 Prevention of upsets in the waste water biotreater

Description

Water effluents from MTBE and TAME production contain releases of methanol, formic acid and ethers. These compounds or their degradation products can be toxic for the fauna of the biotreater. Therefore, high concentrations of these components need to be prevented from entering the bioreactor. This can be easily controlled by the use of a storage tank or by the planning of production in order to dose the right flow to the waste water treatment.

Achieved environmental benefits

The methanol, formic acid and ethers content of the waste water generated in the etherification processes need to be controlled to prevent upsets in the waste water biotreater.

Applicability

Fully applicable.

Economics

The implementation of this technique is not expensive.

Driving force for implementation

To avoid upsets of the biotreater.

Reference literature

[210, Shawcross 2000].

4.11.3 Prevention of leaking of water-soluble compounds

Description

Ethers produced in the etherification processes are highly soluble in water. If they leak, they may contaminate the soil, rainwater and groundwater. This may be a part of a programme for prevention, detection and control of contamination of soil and groundwater (see Section 4.25.1).

Achieved environmental benefits

Reduction of the risk of contamination of water by ethers and alcohols used in these processes.

Driving force for implementation

To avoid contamination of groundwater and surface water by ethers.

Reference literature

[247, FEI 2001].

4.12 Gas separation processes

The gas separation process is relatively simple and the temperature levels are not high enough to create the opportunity for steam generation. No great efficiency improvements are to be expected within a gas plant, but heat integration with upstream plants will normally make use of e.g. reboiling heat available from upstream plant streams, saving direct heating capacity in the gas separation plant. More information on energy management is available in Section 4.15.1.2.

4.12.1 Fugitive emissions reduction

Description

Gas plants process light compounds and are consequently more likely to produce fugitive emissions. The use of dual mechanical seals on pumps, compressors and agitators can reduce VOC emissions. Use of low-leaking valves also can contribute to reducing VOC emissions. This topic is described as an integrated measure within Section 4.23.6.1 as fugitive emissions occur in all refinery processes, but it is mentioned here explicitly because the light compounds used lead to a relatively high level of fugitive emissions.

Achieved environmental benefits

By applying these techniques, fugitive emissions such as VOCs, H₂S and other sulphur compounds can be reduced considerably.

Cross-media effects

See Section 4.23.6.1.

Operational data

See Section 4.23.6.1.

Applicability

See Section 4.23.6.1.

Economics

See Section 4.23.6.1.

Driving force for implementation

To reduce product loss.

Example plants

Programmes of minimisation of VOC emissions can be found in many European and non-European refineries.

Reference literature

See Section 4.23.6.1.

4.12.2 Prevention of emissions of LPG odorant

The storage and handling of odorants used in LPG production is covered in the EFS BREF [5, COM 2006]. However, the dosing of odorant to the LPG product needs to be handled in a proper way to prevent emissions to the environment. This technique is included in Section 2.21.

4.13 Hydrogen-consuming processes

4.13.1 Hydrodesulphurisation processes

Description

See Section 2.13.

Achieved environmental benefits

The reduction of sulphur content of the different fractions. Modern techniques can reduce the sulphur content of distillates to less than 10 ppm. For example, the application of one-step hydration by means of a Co/Mo catalyst (30 – 40 bar) to middle distillates reduces the sulphur content by more than 90 % (down to some 100 ppm), depending on the product, the S content of the feed, and the reaction conditions. If demand for diesel fuel increases, additional compounds (e.g. LCO from the FCC) have to be used in its production. However, these feedstocks contain a variety of aromatic compounds, which have to be hydrated under severe conditions (high temperature, high pressure, highly active catalysts, two-step processes).

Current diesel specifications can be met in conventional single-stage hydrotreating units by lowering liquid hourly space velocity (LHSV) from 3.7 in conventional units to 0.8 – 1.1, by implementing a reactor in series to the existing ones and applying the latest catalyst generation available for gas oil hydrotreating units. Processing a Russian export blend with 1.3 % w/w S and an intermediate sulphur content ahead of the final desulphurisation unit of 0.12 % S, a final sulphur content of 8 ppm S in the raffinate can be achieved during normal operation.

Cross-media effects

Energy consumption, waste generation, effluent water and air emissions.

Operational data

Gas oil hydrotreating units need the additional measure of a high-pressure amine washer in the hydrogen recycle stream to maintain hydrogen purity in the recycle stream with hydrocarbons from fresh feed. The unit will operate at 45 bar, utilising 40 Nm³ hydrogen/t of gas oil feed and anticipating a run length of 30 months.

Applicability

Applicable to distillates from naphtha to heavy residues.

Economics

The estimated installation costs for a reduced-crude desulphurisation process (based on 132 m³/h unit) is EUR 47 million. Another estimated investment summary for a residue desulphurisation system hydrotreater to prepare residue fluid catalytic cracking feed is shown below.

| | |
|--|------|
| Feed rate, Mt/yr | 3.8 |
| Run length, days | 335 |
| Operating factor | 0.92 |
| On-plot investment, EUR million | 272 |
| Total off-plot cost (30 % of on-plot), EUR million | 82 |
| Catalyst cost per charge, EUR million | 10 |
| NB Basis: 2nd quarter 1995 US Gulf Coast | |

Driving force for implementation

To reduce the sulphur content of the feedstock to achieve EU specifications: the current value for sulphur is 10 mg/kg (10 ppm) according to Directive 2009/30/EC.

Example plants

Many desulphurisation processes exist in refineries.

Reference literature

[175, Meyers 1997].

4.13.2 Catalytic distillation

Description

Catalytic distillation for desulphurisation of gasoline in a two-stage process.

Achieved environmental benefits

Reductions of more than 95 % of sulphur content in FCC gasoline containing 1 800 ppm of sulphur have been achieved. This type of technique consumes less energy than traditional desulphurisation processes.

Cross-media effects

Energy consumption, waste generation, effluent water and air emissions.

Applicability

Fully applicable. This technique may also be used for the reduction of benzene in the reformat.

Economics

A two-stage process is designed to treat 7 950 m³/d of FCC gasoline containing 1 800 ppm of sulphur. Its efficiency has been reported as 95 % and its investment costs are approximately EUR 20 million.

Driving force for implementation

To reduce the sulphur content of gasoline to reach EU specifications: the current value for sulphur is 10 mg/kg (or ppm) according to Directive 2009/30/EC.

Example plants

At least one catalytic distillation plant for desulphurisation of 7 950 m³/d of FCC gasoline is available in Europe. In 2010, in the Russian Federation, a 1.26 Mt/yr FCC unit was designed with a catalytic distillation patented process to meet Euro-5 emissions requirements.

Reference literature

[191, UBA Austria 1998].

4.13.3 On-stream catalyst replacement technology for processing high-metal feeds

Description

While the main objective of this process is to extend catalyst life in a downstream fixed bed reactor by maintaining high hydrodemetallisation performance, the catalyst also achieves high hydrodesulphurisation/hydrodemetallisation and hydrodesulphurisation Conradson carbon removal/hydrodemetallisation activity ratios.

Achieved environmental benefits

On-stream catalyst replacement technology improves the residual desulphurisation in the refinery, thereby decreasing the waste generation.

Operational data

The reactor typically operates at 390 °C and 138 bar (2 000 psi).

Applicability

Fully applicable.

Driving force for implementation

To extend the catalyst life of the hydrotreatment processes.

Example plants

Until 1997, there were 15 on-stream catalyst replacement techniques worldwide.

Reference literature

[175, Meyers 1997].

4.13.4 Hydrogenation of light dienes

Description

The hydrogenation of light dienes serves the purpose of producing a more stable refinery stream, reducing upstream gum formation. The process converts dienes into useful olefins. For more information, see Section 2.13.

Achieved environmental benefits

The process helps reduce acid losses in downstream processes (e.g. alkylation). Typical product diene levels from the selective hydrogenation process unit may range from 25 to 1 ppm.

Cross-media effects

Low energy consumption.

Operational data

Low-temperature, liquid phase operation means that no utilities are required in most cases if the feed and hydrogen are both available at suitable conditions. Heating or cooling duties are limited to cases with relatively high diene concentrations in the feed. Commercial operation for a period of more than two years without the need to regenerate or replace the catalyst is typical.

Applicability

The design of the unit is simple. Most of the units are designed for diene reduction to less than 5 ppm in the product.

Economics

The design of the units is simple and requires low capital and nominal operating costs. The cost of the catalyst is low compared with the installation cost. The capital investment, including the catalyst for the unit is small, usually within the range of EUR 0.6 million – 1.2 million. The investment based on a recent project is some EUR 3 million for a plant of 100 000 t/yr capacity.

Driving force for implementation

To reduce gum formation in downstream operations. The flexibility and minimal cost of this technique make the unit a valuable processing tool.

Reference literature

[175, Meyers 1997], [204, Canales 2000].

4.14 Hydrogen production

For SO₂ emissions reduction, hydrogen gains increasing importance as a key reacting agent for the supply of hydrotreating units that are now crucial to the desulphurisation and upgrading of intermediate feedstocks and final products

Hydrogen production using a hydrocarbon-rich feedstock requires, as a first step, the conversion of the feedstock into a carbon oxides- and hydrogen-rich synthesis gas. The synthesis gas generation can be conducted by different techniques, such as steam reforming (see Section 4.14.1), gas-heated reforming (GHR) (see Section 4.14.2) and partial oxidation (see Section 4.14.3). An additional purification step is then needed (see Section 4.14.4). Figure 4.40 shows the H₂/CO ratio for various hydrogen production techniques available.

As mentioned in Section 2.14, the production of hydrogen is not exclusive to the refinery sector. Therefore the sector-specific information contained in this chapter can be completed as necessary by the information available in the other BREF documents, e.g. LVIC-AAF [92, COM 2007].

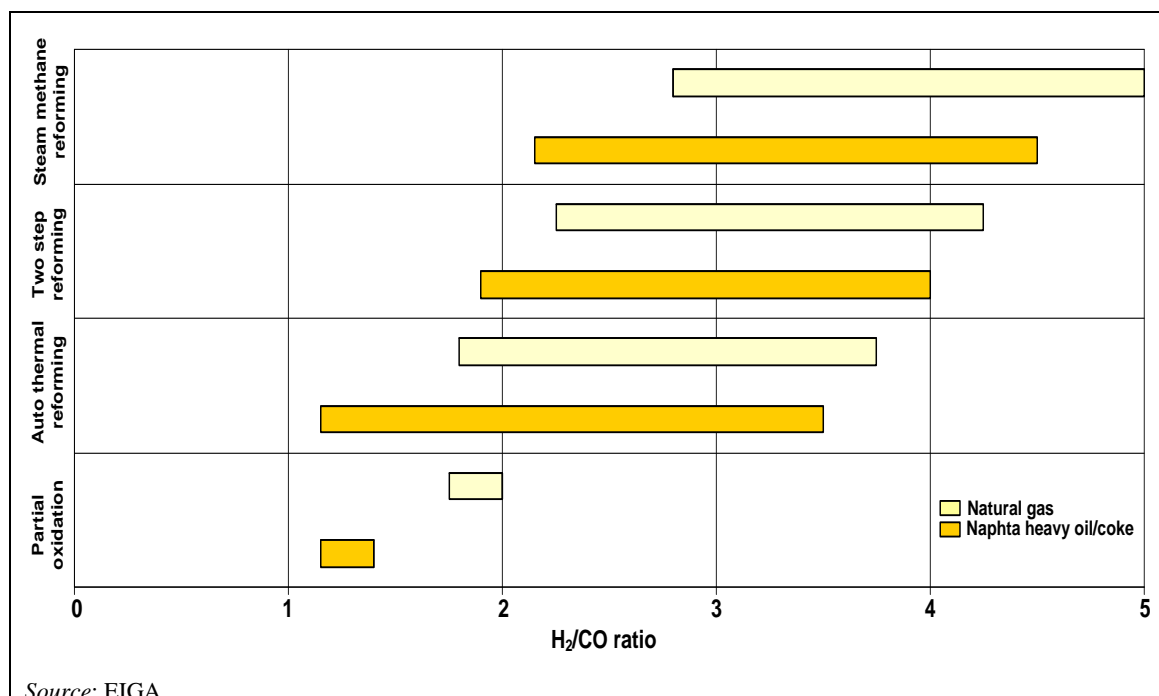


Figure 4.40: H₂/CO ratio for hydrogen production processes available in a refinery

4.14.1 Steam methane reforming

Description

A description of this most commonly used process is given in Section 2.14.

The steam reformer has to supply a large amount of heat at a high temperature for the steam reforming reaction by burning fuel, with the result that a large amount of heat is potentially lost in the flue-gas. As a result, many refineries recover heat as part of their heat integration. However, the values displayed in Figure 4.40 do not take into consideration, as a more general approach, the potential reduction of air emissions that can be achieved from co-production synergies. All of the processes in Figure 4.40 can be used within a refinery to export steam as a valuable product, thereby eliminating the need for dedicated steam production elsewhere and translating directly into energy and CO₂ emissions savings. Furthermore, if there are CO₂ customers there may be some demand such as from agriculture, the food and beverage industry,

or other chemical facilities nearby, and there may be demand for carbon dioxide which can be productively used instead of being emitted as CO₂.

Achieved environmental benefits

- Either exclusively or primarily as a hydrogen production process, steam methane reforming is intrinsically advantageous from both a product yield and an energy consumption point of view (see Figure 4.40 showing product yield ranges, as hydrogen to carbon monoxide ratio, for different processes). In addition, steam methane reforming reduces the potential for CO₂ emissions with its requirement for lighter feedstocks.
- Steam methane reforming of natural gas typically has a small carbon footprint. When available, maximising the use of external methane imported to the refinery for hydrogen production instead of thermal power generation could be seen as a preferable option when hydrogen production needs to be increased.
- Steam methane reforming typically requires 10–15 % excess air with the minimum value being limited by safety considerations. This relatively small quantity is an intrinsic primary measure for the reduction of NO_x emissions.
- As it is a closed-loop process, the obligation to thoroughly monitor the excess O₂ and/or CO content in the SMR flue-gas also provides the opportunity for the enhanced control and reduction of CO and unburnt hydrocarbon emissions.
- The steam methane reforming process requires a very deep desulphurisation of the feed so as to prevent catalyst poisoning. As a result, the tail gas from the PSA is virtually free of sulphur. As it forms up to 90 % of the fuel, SO_x emissions are correspondingly reduced and will only depend on the sulphur content of the supplementary fuel.

Cross-media effects

The choice of heat recovery system can have a major effect on NO_x production, since both the amount of fuel fired and the flame temperature will be affected. Preheating combustion air will reduce firing, but since NO_x formation increases with flame temperature, there will be an overall increase of NO_x concentration, limiting the overall NO_x mass flow reduction. Other methods of reducing firing, such as pre-reforming or gas-heated steam reforming (see Section 4.14.2), do not affect the flame temperature and will reduce the overall required firing duty without increasing the NO_x concentration, and therefore will reduce NO_x production. The production of CO₂ is also important. For every tonne of H₂ produced, some 10 tonnes of CO₂ are also produced including the amount related to steam production. This value may vary widely depending upon the strategy for conducting the steam production. Other impacts, such as SO_x or water emissions, are minimal, because low-sulphur fuel is typically used.

Operational data

The combination of high temperature and pressure imposes severe demands on the steam reformer tubes, which must be fabricated from expensive alloys. The furnace box must be large to obtain the high rates of heat transfer from the flue-gas to the tubes. These combined factors make the steam reformer the largest and single most expensive piece of equipment in a hydrogen plant. The large size of the unit means that it takes a long time to heat up and cool down, and this makes it the most time-consuming part of the start-up and shutdown procedure.

Applicability

Fully applicable.

Economics

The operating expenses are dependent on the type of feed used and a typical specific energy consumption (feed + fuel – export steam) range is between 3 and 3.4 Gcal/1 000 Nm³ (12.5 – 14.2 kJ/Nm³).

Driving force for implementation

The need for additional sources of hydrogen is increasingly a crucial requirement for maximising the hydrotreatment capacity in the refinery and meeting SO_x challenges and the sulphur level enforced in the final product quality standards.

Example plants

There are many examples of steam methane reforming plants in operation associated with European oil refineries.

Reference literature

[56, EIGA 2009], [76, Hydrocarbon processing 2011], [163, FWE 1999].

4.14.2 Gas-heated reforming (GHR)**Description**

The gas-heated reforming (GHR) technique generally uses a compact unit heated by high-temperature waste heat from the raw synthesis gas, often by means of a heat exchanger-type reactor downstream of the conventional synthesis gas generator. In other examples, the GHR can also be fully integrated into the synthesis gas generator.

The recovered heat is used in the GHR to drive the endothermic reforming reactions instead of solely using this heat for steam generation in a steam boiler. Consequently, a hydrogen production plant with a GHR unit produces less excess steam than a conventional synthesis gas production plant based on a steam reformer or partial oxidation reactor.

Achieved environmental benefits

Gas-heated steam reforming reduces the energy consumption of the synthesis gas production process itself. It is especially appropriate for refineries where high-pressure steam is not strictly needed for operating other production units.

Cross-media effects

When GHR is applied, little or even no steam is produced from the hydrogen plant. Depending on the specific configuration of the site energy system, the steam production in other units may need to be increased. The benefits from the application of GHR must then be balanced with the associated steam reduction demanded by the industrial steam network and/or the additional energy consumption and air emissions that would accompany the increase of steam production outside the hydrogen production plant.

Operational data

GHR recovers sensible heat from the process gas to drive the endothermic reforming reaction in an additional reactor. Many different possibilities to design a GHR unit exist, and many only use a small additional feed (i.e. 10 – 20 %) as a fraction of the total feed. The resulting economics can vary widely. One exemplary embodiment of the GHR application is essentially a special heat exchanger filled with highly active catalyst.

The severe operating conditions (high temperature) require very careful design. Because of the higher wall temperatures of the heat exchange surface compared to conventional steam boilers and the reducing gas atmosphere, severe and instantaneous corrosion of particularly high-alloyed materials by the metal dusting corrosion phenomena are highly likely. Besides the risk to operation by failure of the heat exchange equipment, the resulting metal and carbon particles accumulate in the process condensate and can have an impact on the plant operation. Therefore, specific HSE and reliability/availability requirements will have to be taken into account for application of the GHR technology.

The integration of the GHR technology into a synthesis gas plant requires special procedures for start-up, operation and shutdown and consequently requires operational effort to maintain the catalyst lifetime.

Applicability

Fully applicable. However, the application of GHR as a steam reduction process technology must be evaluated against other design options which may include using the excess steam for

power generation or mechanical power in rotating equipment. Gas-heated steam reforming may represent an attractive alternative process technology if high-pressure steam cannot be consumed by other units outside the synthesis gas generation unit.

Economics

Economics depend strongly on the specific site configuration. Because of the severe conditions of gas-heated steam reforming (high temperature, corrosive atmosphere), the typical embodiment as described above - a special heat exchanger filled with highly active catalyst - represents a significant capital expenditure.

Driving force for implementation

Hydrogen is increasingly needed for hydrotreatments performed in the refinery.

Example plants

GHR is a new alternative, already proven commercially for a few applications, e.g. in ammonia and methanol production. As far as refining is concerned, GHR is typically applied to debottleneck existing conventional SMR-based hydrogen plants.

Reference literature

[56, EIGA 2009].

4.14.3 Partial oxidation

Description

The IGCC plant can also function as a hydrogen supplier, in which case hydrogen is removed from the syngas (after the sulphur removal) where the feed reacts at high temperatures with oxygen. For more information see Sections 2.14, 2.10 and 4.10.3.4.

Achieved environmental benefits

Coke gasification

A fixed bed desulphurisation system using regenerable zinc ferrite as the sorbent has been tested as a continuation of the gasification exhaust gas treatment. Sulphur levels of 10 – 20 ppm in the treated gas were achieved in this system. The product gas also contains traces of ammonia (less than 5 %) and hydrogen cyanide (HCN), derivatives of the nitrogen in the feed. Using limestone in the gasifier tends to reduce the level of these components. Ammonia is not removed by zinc ferrite in the external desulphurisation process. If there is any alkali in the feed, some of it may vaporise in the gasifier and may have to be removed by an alkali sorbent or by cooling the gas going to the filter. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm.

Heavy oil gasification

Another environmental benefit of gasification is that it reduces heavy oils which, when used in another way, may pollute the environment much more. See also Section 4.10.3.4.

Cross-media effects

Partial oxidation requires an oxygen plant (95 – 99 % purity), which increases costs.

Operational data

Normally, an IGCC plant includes a water purification section with the following units:

- soot recovery, either by washing with naphtha and recycling of the naphtha/soot mixture to the gasification section and/or by filtration;
- water pretreatment, to remove solids (carbon, metals, salts) by filtration before final treatment in the biological plant, e.g. a grey water treatment (GWT).

Grey water treatment (GWT) is designed to treat water blowdown from a carbon extraction unit with syngas condensate and possibly the amine regeneration overhead system; water from grey water treatment is finally sent to biological treatment. The GWT may employ physical and chemical treatment for cyanide destruction and the removal of heavy metals, followed by a sour water stripper, which removes sulphides, ammonia, and carbon dioxide from the water.

The gaseous streams are totally washed to remove any contaminant and the process normally includes the following ancillary units for gas purification:

- washing with water and sometimes oil to remove soot and particulate;
- reactor for COS or cyanides by hydrolysis;
- sour gas absorbing with amine or equivalent system and the production of elemental sulphur from H₂S in the Claus unit.

Applicability

Relative hydrogen production costs are primarily a function of feedstock cost. The main problem with investment in a gasification plant is its capital and operating cost. To be attractive commercially it usually needs to be undertaken on a large scale. Typical requirements for chemicals production are the generation of more than 200 MW_e of electrical power through IGCC or the use of hydrogen, carbon monoxide and steam on a large scale.

Economics

Generally accepted investment costs for an oil gasification-based combined cycle plant in the 200+ MW_e range are EUR 1 300 – 1 700 per kW installed, with a thermal efficiency of around 40 % and close to 99 % sulphur emission abatement. On average, electrical demand in a refinery is usually less than 80 MW_e, the investment in IGCC often depends on the opportunity to export the surplus of electrical power generated. However, high-pressure steam can also be a valuable gasification product and there are examples of much smaller gasification units that fit in well with a refinery.

Relative hydrogen production costs of the process are primarily a function of feedstock cost. Steam reforming of methane usually produces hydrogen at lower costs than the partial oxidation of fuel oil.

Driving force for implementation

The production of hydrogen costs, the reduction in heavy oils produced, power export and the synthesis gas produced as feed for petrochemistry are the driving forces for the implementation of gas-heated steam reforming.

Example plants

At least five gasification processes are currently running in European refineries.

Reference literature

[175, Meyers 1997], [221, Italy 2000].

4.14.4 Purification of hydrogen

Description

Information about the processes of purification can be found in Section 2.14. Some techniques that may be applied to the hydrogen purification units to achieve better environmental performance are given below.

- Use of several adsorber beds periodically switching the gas flow from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is used as fuel at a convenient location.

- Use of PSA systems only for purification of hydrogen to reduce air emissions.
- Use of the PSA tail gas as refinery fuel gas in the reforming furnace instead of higher C/H ratio fuels.
- Use of membranes technique which can achieve purification ratios of 80 % v/v.

Achieved environmental benefits

Reuse of waste fuel gas as a fuel within the process.

Cross-media effects

Because of the loss of hydrogen to the PSA tail gas, the reformer and front end of a PSA plant are larger than in a wet scrubbing plant. However, a PSA plant uses less process steam and does not require heat for the reboiler. PSA is a high energy consumer due to the high vacuum/pressure systems that it uses.

Operational data

The PSA system is completely automatic and offers a higher purity product. The PSA unit is simpler to operate than a wet scrubbing system, since it has no rotating equipment or circulating solutions. The conventional process produces a hydrogen product of maximum 97 – 98 % v/v purity, while the pressure swing adsorption process produces a very pure hydrogen product between 99.9 % v/v and 99.999 % v/v. The residual constituents of the product gas are mainly methane and less than 10 ppm CO. Some data on the utility consumption of the PSA system are for example: 3 700 Nm³/h with a H₂ content of at least 85 % and a pressure between 37 and 47 bar. Product stream: 2 400 Nm³/h purified H₂ with a concentration of at least 99.5 %, temperature: 45 °C, pressure: 35 bar; waste gas: 1 300 Nm³/h, P: 3 bar, T: 30°C, contains 60 % H₂, 1.4 % H₂S and 40 % C₁-C₆ compounds with higher boiling points.

Driving force for implementation

To purify the hydrogen. The choice between the PSA system and the scrubbing system depends on the product purity required, reliability and process economics. The extra investment for the PSA system for large plant capacities can normally be offset by the lower operating cost. Also, a PSA system will yield a higher H₂ purity.

Example plants

Many examples exist as PSA is commonly used.

Reference literature

[175, Meyers 1997], [182, Ecker 1999], [221, Italy 2000].

4.15 Integrated refinery management

This section is structured in the same way as Chapters 2 and 3 and contains the integrated refinery management activities that are not included in other sections. The first techniques to consider are environmental management activities and other utility management techniques.

4.15.1 Environmental management tools

4.15.1.1 Environmental management system

Description

A formal system to demonstrate compliance with environmental objectives.

Technical description

The Directive defines 'techniques' (under the definition of 'best available techniques') as 'both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned'.

In this respect, an environmental management system (EMS) is a technique allowing operators of installations to address environmental issues in a systematic and demonstrable way. EMSs are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

An EMS focuses the attention of the operator on the environmental performance of the installation; in particular through the application of clear operating procedures for both normal and other than normal operating conditions, and by setting out the associated lines of responsibility.

All effective EMSs incorporate the concept of continuous improvement, meaning that environmental management is an ongoing process, not a project which eventually comes to an end. There are various process designs, but most EMSs are based on the plan-do-check-act cycle (which is widely used in other company management contexts). The cycle is an iterative dynamic model, where the completion of one cycle flows into the beginning of the next (see Figure 4.41).

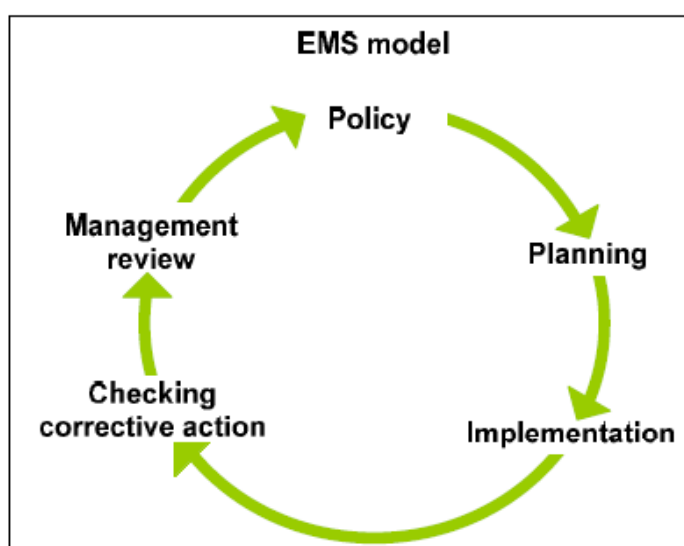


Figure 4.41: Continuous improvement in an EMS model

An EMS can contain the following components:

1. commitment of management, including senior management;
2. definition of an environmental policy that includes the continuous improvement of the installation by the management;
3. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
4. implementation of procedures paying particular attention to:
 - (a) structure and responsibility
 - (b) training, awareness and competence
 - (c) communication
 - (d) employee involvement
 - (e) documentation
 - (f) efficient process control
 - (g) maintenance programmes
 - (h) emergency preparedness and response
 - (i) safeguarding compliance with environmental legislation;
5. checking performance and taking corrective action paying particular attention to:
 - (a) monitoring and measurement - see also the document on the General Principles of Monitoring [46, COM 2003]
 - (b) corrective and preventive action
 - (c) maintenance of records
 - (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
6. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
7. preparation of a regular environmental statement;
8. validation by a certification body or an external EMS verifier;
9. following the development of cleaner technologies;
10. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
11. application of sectorial benchmarking on a regular basis.

Achieved environmental benefits

An EMS promotes and supports the continuous improvement of the environmental performance of the installation. If the installation already has a good overall environmental performance, an EMS helps the operator to maintain the high performance level.

Environmental performance and operational data

No data.

Cross-media effects

None reported. The systematic analysis of the initial environmental impacts and scope for improvements in the context of the EMS sets the basis for assessing the best solutions for all environmental media.

Technical considerations relevant to applicability

The components described above can typically be applied to all installations within the scope of this document. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

Economics

It is difficult to determine accurately the costs and economic benefits of introducing and maintaining a good EMS. There are also economic benefits that are the result of using an EMS and these vary widely from sector to sector.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum.

Driving force for implementation

The driving forces for the implementation of an EMS include:

- improved environmental performance;
- improved insight into the environmental aspects of the company which can be used to fulfil the environmental requirements of customers, regulatory authorities, banks, insurance companies or other stakeholders (e.g. people living or working in the vicinity of the installation);
- improved basis for decision-making;
- improved motivation of personnel (e.g. managers can have confidence that environmental impacts are controlled and employees can feel that they are working for an environmentally responsible company);
- additional opportunities for operational cost reduction and product quality improvement;
- improved company image;
- reduced liability, insurance and non-compliance costs.

Example plants

EMSs are applied in a number of installations throughout the EU.

Reference literature

[93, DG Environment 2010], [94, ISO 2010], [95, ISO 2004], [96, Reg.1221/2009].

4.15.1.2 Energy conservation techniques

A concerted and well-managed effort based on an integrated approach to reduce energy use, improve operations, maintain good housekeeping, and management and selective investments are the best practices worth highlighting here. There follows a list of techniques that are considered for the determination of BAT in the refinery sector. As can be seen, some of them are related to others in some way.

| Description of the technique | Performance and remarks |
|---|---|
| To have a management focus on energy | To ensure that decisions are made on a process-integrated basis |
| To instigate an energy consumption reporting system | To measure progress and ensure that targets are met |
| To instigate an incentive scheme for energy savings | To promote identification of improvement areas |
| To carry out energy audits on a regular basis | To ensure activities are in conformance with instructions |
| To have a formal energy consumption reduction plan | To set targets and strategies for improvements |
| To carry out combustion improvement campaigns | To identify areas of improvement (e.g. air/fuel ratio, stack temperature, burner configuration, furnace design) |
| To participate in ranking/benchmarking activities in energy consumption | Verification by an independent body |
| To review the integration between and within units and systems | Heat integration between units in the refinery can be suboptimal. 'Pinch' studies |

Achieved environmental benefits

All measures to reduce energy consumption will result in a reduction of all emissions to air, including CO₂. Any energy conservation action has an impact on pollution due to the marginal fuel consumption.

Applicability

Especially applicable to those refineries with very high specific energy consumption (see Section 3.10.1).

Reference literature

[168, VROM 1999], [221, Italy 2000].

4.15.2 Production planning and control

Description

To ensure the full use of key abatement techniques (for both availability and capacity), some procedures can be defined for specific conditions where the operating parameters of a waste gas or waste treatment system may have a significant effect on the overall achieved removal efficiency (e.g. quantity of alkaline reagent, working temperature, waste gas flow, bypass operations).

Special procedures can be defined for specific operating conditions, in particular:

- start-up or shutdown operations;
- other special operations which could affect the proper functioning of the system (e.g. regular and extraordinary maintenance work and cleaning operations of the furnace and/or of the waste gas treatment system, or severe production change);
- insufficient waste gas flow or temperature which prevents the use of the system at full capacity.

4.15.3 Safety management

Safety management in a refinery is mainly addressed through the requirements of the Seveso II and Seveso III Directives (respectively 96/82/CE and 2012/18/EU).

4.15.4 Water management

4.15.4.1 Water stream integration (WSI)

Description

Similar to the identification of energy-saving opportunities, water pinch studies can be carried out to identify process water integration options and water reduction and reuse opportunities. In most refineries, some internal water streams are commonly used as desalter wash water, such as condensate water and steam-stripped sour water. There is scope for increased water reduction and reuse in refineries, which will lead to reduced size and costs of both water make-up and end-of-pipe treatment facilities.

Technical description

Purpose and principle

The purpose of water stream integration (WSI) is the reduction of process water produced for final treatment prior to discharge, in order to save operational costs. It saves high-quality potable and demineralised water, which can be expensive at some locations; it reduces the size, investment and running costs of the water supply and effluent treatment facilities. Moreover, it reduces the size and the environmental impact of effluent discharges.

The principle of WSI is to use, when possible, prevention, reduction, recycling and reuse of process water, rainwater, cooling water and sometimes contaminated groundwater with the aim of reducing the amount of process water for end-of-pipe treatment. WSI needs to be carried out as part of a water master plan for the refinery. This plan aims at the optimisation of the use and reuse of all water streams in the refinery.

The water used for the process in a refinery is of the magnitude of 0.1 to 0.6 m³ per tonne of feed. Some techniques to consider for the reduction of fresh water consumption can be, but are not limited to, the following:

- reusing unstripped/stripped sour water as wash water,
- use of rainwater as process water.

Concept description

The concept or methodology to design an effluent/water integration system for a refinery is to take an inventory of water demand and effluent production for each refinery unit operation and to assess the water losses. This inventory provides the water balance across the refinery. It is recommended to visualise the water balance by a block scheme as presented as an example in Figure 4.42. The next step is to identify all possibilities to reduce the amount of water required and to reuse as much as possible by matching (quantity and quality) effluents by means of a water optimisation scheme. This 'water pinch' methodology includes giving consideration to the reuse of treated effluent. The WSI concept aims at 'closing the water loop'.

WSI is mainly dependent on the refinery configuration, location, availability and type of raw water, the crude quality and the level of desalting required, the cost of potable water, the type of cooling water system and the availability of rainwater. Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available as well as a number of standard possibilities for water reduction and reuse.

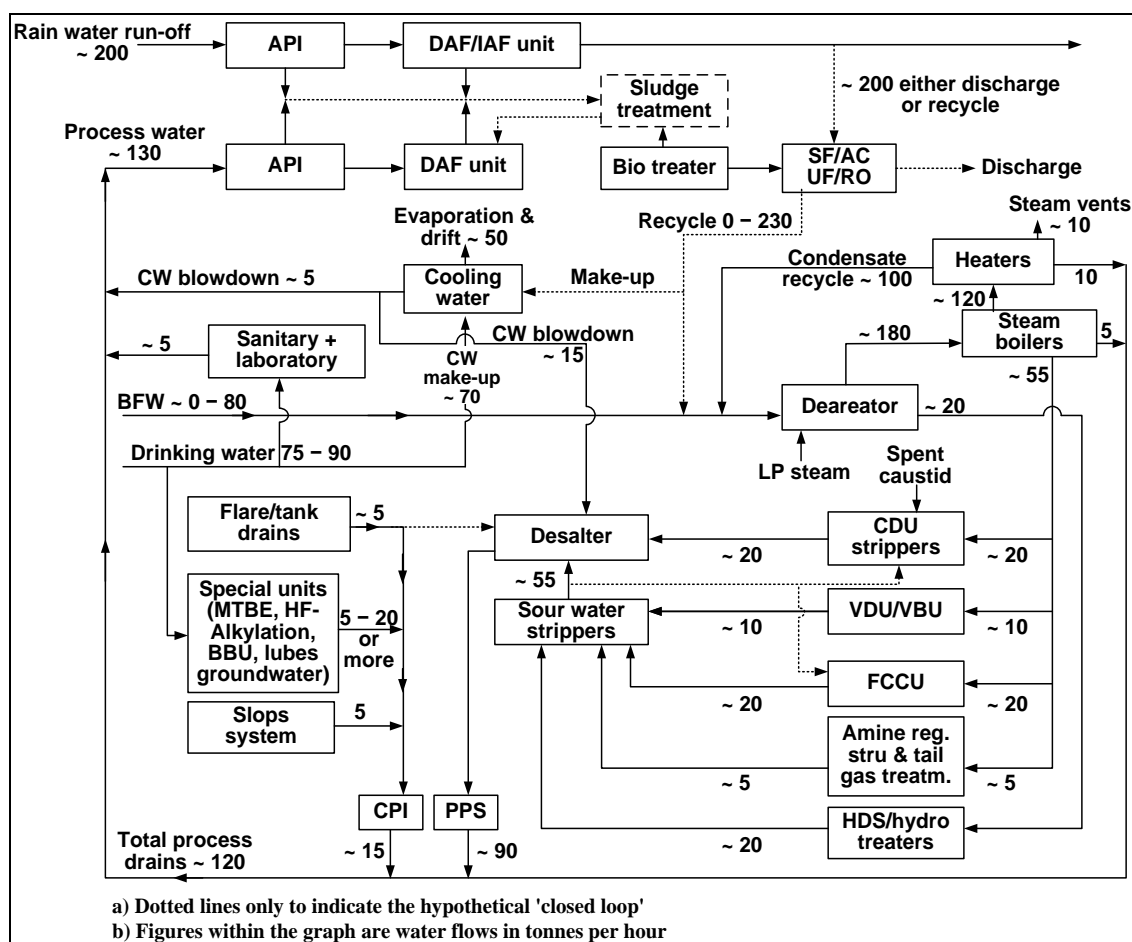


Figure 4.42: Example of a process water integration scheme for a catalytic cracker refinery configuration (10 Mt/yr)

Achieved environmental benefits

Water stream integration mainly aims at reducing the consumption of fresh water. The environmental implications of the conceptual approach of a process water integration scheme are favourable. Enclosed systems and closed-water loops limit the hydrocarbon emissions to air and discharges to surface water, and also lead to the reduced generation of waste in the form of sludges. The quantification of the reduction of the water used (and products lost) vary from location to location but can be substantial (>50 %).

Environmental performance and operational data

Reducing the volume of water discharged reduces the size of the effluent treatment plant required, the amount of energy and chemicals used, and the quantity of pollutants discharged to the environment. Data on actual fresh water usage are included in Section 3.1.1.2, Table 3.3 and Section 3.15. Based on the TWG data collection, specific consumption mainly ranges between 0.2 and 25 m³/t of feedstock, the largest part still being used for cooling and returned to fresh-water bodies.

Cross-media effects

Reducing the water volume can lead to increased pollutants concentrations entering the waste water treatment plant but the process, if properly designed, can generally deal with this issue. This rise might put the value for one or several priority substances beyond the environmental quality standard (EQS) of the Water Framework Directive (WFD). Specific attention should be paid to these cases and could justify a specific study.

Technical considerations relevant to applicability

Generally applicable to existing plants, but when included in the initial design it can lead to even higher efficiency.

Economics

No data.

Driving force for implementation

The reduction of fresh water use is a goal for most refineries for two main reasons. First, fresh water, particularly high-quality water, is a valuable resource which in many parts of Europe is becoming increasingly scarce. Where water of a lower quality is used, treatment to acceptable standards also requires the use of energy and chemicals. Secondly, water used has to be discharged.

Example plants

A newly built refinery in Thailand generates only 40 t/h process water at a crude throughput of 8 Mt/yr due to such an approach. Values of 0.5 m³ per tonne of crude oil have been also achieved within Europe.

Reference literature

[77, REF TWG 2010], [164, Noyes 1993], [167, VDI 2000], [168, VROM 1999], [207, TWG 2001].

4.15.4.2 Water and drainage system**Description**

Flexibility is needed in water and drainage systems to cope with changing circumstances, such as sudden rainfall, firefighting, process upsets, process changes, additional plants, capacity extensions and new regulatory demands. A basis for integrated water management is also needed, including spill prevention and potential reuse of water streams without or after treatment. The principle is based on a thorough qualitative and quantitative analysis of the various water and effluent streams, the assessment for reuse potential with maximum reliability and environmental protection. A flexible water and drainage design allows for water integration and allows for short-term and long-term changes at optimised cost. An enclosed sewerage system for the transfer of contaminated water from tanks and processes to separation facilities is also a technique to consider.

Technical description

A water and drainage system of an industrial site is the result of a conceptual design of many unit operations lined up in such a way that water management can be optimised. The basis of the concept is segregation of the different water streams into oil-free water streams, accidentally oil-contaminated (AOC) streams and continuously oil-contaminated (COC) streams. The latter may be subdivided into low- and high-BOD streams with the possibility for biotreatment, effluent polishing and reuse (see Figure 4.43).

The application of the segregation concept takes a certain level of housekeeping and operational discipline into account. The decision to choose a different route for a certain type of effluent would be based on the monitoring of water qualities, both of internal streams and the collective discharge. The environmental performance and the effluent management of the refinery require a constant level of alertness and dedication, sufficient training and motivating instructions and an extensive monitoring (sampling and analysis) scheme. The concern is mainly with the first flush, which entails the collection, separation and treatment of the first charge of rainwater from the potentially contaminated refinery surface. After the first flush, the rest of the rainwater is collected, analysed and discharged without treatment, if acceptable.

Achieved environmental benefits

Prevention of pollution due to discharge without appropriate treatment of water coming from the whole refinery drainage system.

Environmental performance and operational data

No data.

Cross-media effects

Energy requirements are mainly for pumping the waste waters and are system- and site-dependent.

Technical considerations relevant to applicability

A number of elements of the current design approach for a new water and drainage system can be considered for implementation in existing refineries. However, as the overall drainage systems of old refineries have remained unchanged, the applicability of segregation of drainage streams may be limited.

Economics

No data.

Driving force for implementation

Source reduction and spill prevention by good housekeeping are also essential elements for VOC and odour emission reduction at CPI, API, DAF units and biotreaters.

Example plants

Not many refineries have segregated process water and rainwater run-off. If they do, these streams are routed to separate and dedicated treatment systems. The extent of segregation varies from refinery to refinery (by design or retrofit). Most refineries use stripped sour water and/or some condensate streams as desalter wash water (see Section 4.9). Reuse of treated effluent (biotreatment, filtration followed by reverse osmosis) as a source for boiler feed water is technically feasible. Reuse of treated effluent as cooling water make-up is done at several locations. First flush treatment is applied in several refineries. Some refineries employ an H₂S oxidation tank to prevent toxic and odorous emissions from process water prior to DAF and biotreatment.

Figure 4.43 shows a block diagram of an example of an optimised water/effluent routing for a refinery.

Reference literature

[148, Irish EPA 1993], [168, VROM 1999], [223, Bakker et al.1994].

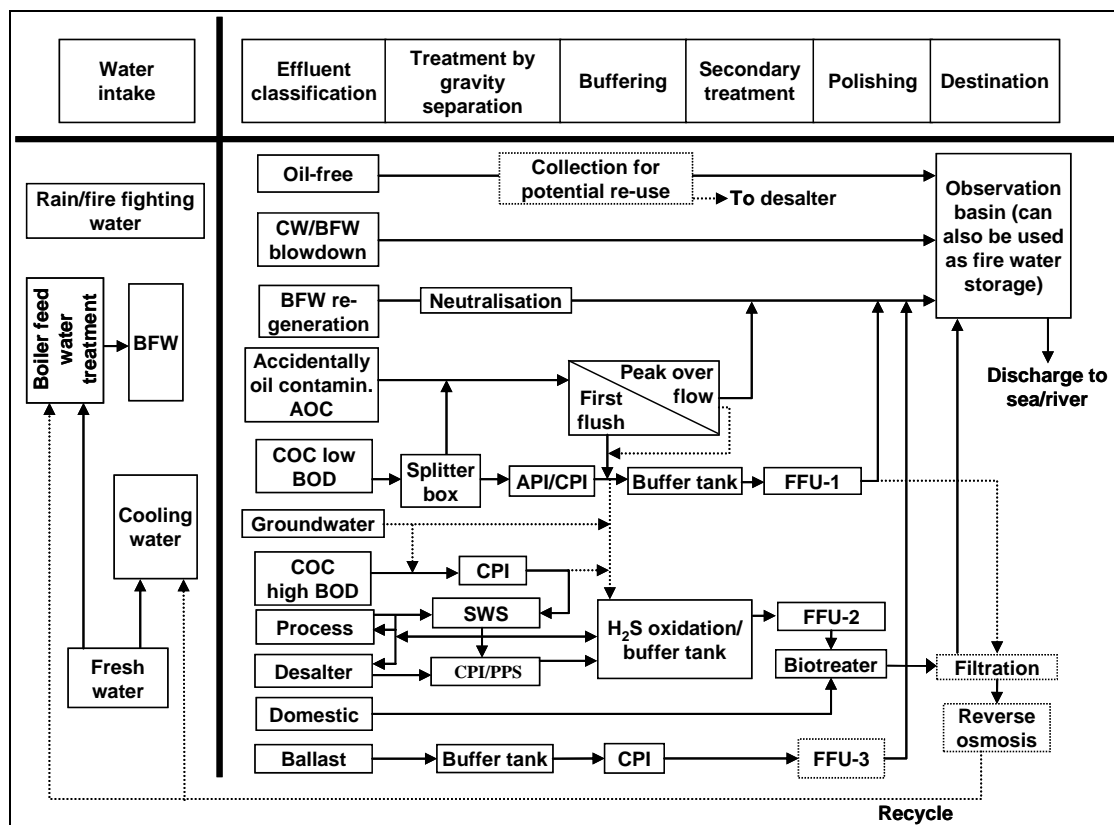


Figure 4.43: Block diagram of an example of an optimised water/effluent routing for a refinery

4.15.4.3 Rainwater

Some techniques that may be applied to rainwater are given below.

- Surface water run-off or rainwater can be segregated into oil-free, accidentally oil-contaminated, and continuously oil-contaminated effluents. These effluents may require treatment. Rainwater on contaminated surfaces may lead to effluent to be treated in a CPI/API.
- In specific situations, rainwater may be a useful source of raw water for the preparation of process water make-up, boiler feed water and cooling water.
- Some refineries have segregated effluent and drainage systems. In a number of refineries, the water and drainage system includes a segregation of process water, condensate blowdowns, rainwater and cooling water, in order to reduce the environmental impact of effluent discharges at minimum cost. Moreover, adequate process water integration and water management measures will include a review of all options to recycle water streams, with the aim of achieving a significant reduction of end-of-pipe treatment. Segregation of the process water discharges, surface water run-off, cooling water and boiler feed water blowdowns and other effluents may be considered. Separation of storm water and other effluents of different origins in order to permit appropriate treatment options may be considered. In some cases, retrofitting costs can be very high.

Reference literature

[164, Noyes 1993], [168, VROM 1999].

4.15.4.4 Ballast water

Ballast water is typically discharged at a very high rate, provoking the generation of high volume waste water peaks, which can contain high salt concentrations (seawater), and a high oil content. It can easily lead to an upset of existing effluent treatment systems. Therefore the use of ballast water tanks is an important equalisation tool for feeding the water in a controlled way to the waste water treatment plant, if the COD is lower than 100 ppm. Because of this, (and because jetties are often remote from the rest of the refinery), ballast water is often treated in a specific separate plant. As more and more crude tankers are equipped with double hulls, the ballast water problem is slowly being phased out.

4.15.4.5 Firefighting water

Some techniques to consider are:

- The firefighting water system can sometimes be a water reuse sink within the refinery.
- Provision should be made to reduce the potential for pollution as a result of firefighting activities (e.g. to collect firefighting water in a basin). Serious pollution can be caused by the release of firefighting water in an emergency. Design of Containment Systems for the Prevention of Water Pollution from Industrial Accidents can be found in the Construction Industry Research and Information Association Report 164 1996.

4.15.4.6 Priority substance-driven management

Description

Within the framework of European legislation (specifically Directive 2000/60/EC, the Water Framework Directive), this technique is a strategy to identify and reduce the water releases of substances classified as 'priority substances'.

An appropriate strategy could be implemented and include the following steps.

- Establishing a list of substances that may be released by the refinery sites.
- Setting sampling prescriptions for monitoring normal operating conditions (temporary or permanent plan).
- Determining the most relevant period for a temporary monitoring plan, e.g. a six-monthly or yearly if the values are very low, and carrying it out.
- Analysing the results and establishing a concrete action plan for reducing emissions of the corresponding substances to be included in the EMS. This could result, for example, in adding substances to the regulatory monitoring plan.

Achieved environmental benefits

According to the Water Framework Directive, progressive reduction of priority substances discharge from refineries. For priority hazardous substances, cessation or phasing out of discharges.

Operational data

Based on the results from a French monitoring campaign, the following table may be used to determine the substances to be monitored monthly during a six-month transitory plan. In the last step, a relevant list of substances to monitor for each plant will be defined. When appropriate, specific actions will have to be carried out by operators in order to achieve reduction under the control of the local authorities.

Table 4.62: Example of hazardous substances tracking in refineries' discharges

| Substances | CAS ⁽¹⁾ number | WFD ⁽²⁾ number | Limit of quantification (µg/l) | Transitory monitoring ⁽³⁾ |
|----------------------------|---------------------------|---------------------------|--------------------------------|--|
| Benzene | 71 – 43 – 2 | 4 | 1 | Systematic for benzene production sites only |
| Xylenes (o, m, p) | 1 330 – 20 – 7 | | 2 | Systematic |
| Anthracene | 120 – 12 – 7 | 2 | 0.01 | Systematic |
| Fluoranthene | 206 – 44 – 0 | 15 | 0.01 | Systematic |
| Naphthalene | 91 – 20 – 3 | 22 | 0.05 | Systematic |
| Benzo (a) pyrene | 50 – 32 – 8 | 28 | 0.01 | Systematic |
| Benzo (b) fluoranthene | 205 – 99 – 2 | 28 | 0.01 | Systematic |
| Benzo (g, h, i) perylene | 191 – 24 – 2 | 28 | 0.01 | Systematic |
| Benzo (k) fluoranthene | 207 – 08 – 9 | 28 | 0.01 | Systematic |
| Indeno (1, 2, 3-cd) pyrene | 193 – 39 – 5 | 28 | 0.01 | Systematic |
| Cadmium and compounds | 7 440 – 43 – 9 | 6 | 2 | Systematic |
| Lead and compounds | 7 439 – 92 – 1 | 20 | 5 | Systematic |
| Mercury and compounds | 7 439 – 97 – 8 | 21 | 0.5 | Systematic |
| Nickel and compounds | 7 440 – 02 – 0 | 23 | 10 | Systematic |
| Arsenic and compounds | 7 440 – 38 – 2 | | 5 | Systematic |
| Zinc and compounds | 7 440 – 66 – 6 | | 10 | Systematic |
| Copper and compounds | 7 440 – 50 – 8 | | 5 | Systematic |
| Chromium and compounds | 7 440 – 47 – 3 | | 5 | Systematic |
| Biphenyl | 92 – 52 – 4 | | 0.05 | Additional |
| Tributyl phosphate | 126 – 73 – 8 | | 0.1 | Additional |
| Hexachlorobenzene | 118 – 74 – 1 | 16 | 0.01 | Additional |
| Chloroform | 67 – 66 – 3 | 32 | 1 | Additional |
| Perchloroethylene | 127 – 18 – 4 | | 0.5 | Additional |

⁽¹⁾ CAS: Chemical Abstract Service.
⁽²⁾ WFD: Water Framework Directive.
⁽³⁾ Additional means case-by-case approach.
Source: [263, TWG 2010] FR French Strategy to reduce discharges of dangerous substances.

Applicability

Applicable to existing installations.

Economics

Costs may vary greatly depending on the total number of substances monitored and on the duration of the transitory monitoring programme put in place, which are very site-specific. It may be necessary in some cases (e.g. where ubiquitous substances are detected) to also measure these substances in the raw water uptaken by the refinery, potentially increasing the number of samples and analyses. The cost for an analysis of a dozen substances is estimated (in 2010) as between EUR 1 500 and 3 000.

Driving force for implementation

EU legislation.

Example plants

In France, 13 refineries were concerned.

4.15.5 Site-level management of air emissions: the 'bubble approach'

Description

Refineries meet some or all of their energy needs with a variety of gaseous and liquid fuels that are by-products of the various processes. In this respect, refineries differ from other industries that generally buy all their specified fuels from outside. Another particularity of the refining sector is the recognised complexity of refineries. Aspects of this complexity include, in a modern refinery, numerous emission points interrelationships between feedstock, types of processes and variations in different operating conditions in relation to product slate and product quality requirements. Furthermore, a refinery operates using, at different plants and at different times, the various fuels it produces in-house.

One of the most used techniques for site-level management of air emissions is known as the 'bubble approach' and can be described as follows.

The 'bubble approach' is a generic tool for expressing and comparing the level of emissions achieved or expected at refinery site level, from a clearly identified set of combustion and process units, and for a given substance or parameter. As represented in Figure 4.44, this approach consists of considering all concerned emissions together, as emitted through a 'virtual single stack'.



Figure 4.44: The single 'virtual chimney stack' of a 'bubble approach'

This approach is considered especially suitable to oil refining, where some flexibility is needed for expressing or evaluating the environmental performance at the site level. This flexibility is notably justified by the following factors:

- the recognised complexity of refining sites, with multiplicity of combustion and process units, often interlinked for their feedstock and energy supply;
- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received;
- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements;
- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls have been duly justified as not being possible and have to be compensated elsewhere.

Based on the exchange of information within the TWG, a proposal for a harmonised methodology for the bubble calculation is provided in Annex 8.6. This example enables to set a site-level air emission value based on BAT. It provides a method for calculations of SO₂ and NO_x equivalent concentration (mg/Nm³) and can also be used for setting global loads (e.g. tonnes per year). This approach assumes, as a prior condition, that the global result on the environment should be at least as efficient as if BAT-AELs were achieved for every individual process.

This ensemble of techniques consists of setting, in the refinery management system, appropriate targets, dedicated procedures and specific monitoring instruments in order to allow the operator:

- to set clear emission targets at the site level;
- to permanently monitor the site environmental performance against the set targets;
- to optimise possible site energy requirements together with their related air emissions;
- to identify the most cost-effective places for the application of new primary or end-of-pipe techniques for further reduced emissions;
- to better prepare and anticipate retrofitting difficulties;
- to maximise the availability and stability of abatement processes and equipment.

Technical description

Focusing on the most used technique for site-level management the ‘bubble approach’, as described in Annex 8.6, is based on the main items given below.

Bubble perimeter

The exact bubble perimeter to be considered for a given site will depend on the purpose the bubble tool is used for. For the purpose of applying BAT, the proposal methodology provided in Annex 8.6 is designed to cover, as necessary, all sources of permanent emissions of a refinery: i.e. combustion plants, catalytic crackers, sulphur recovery units, coke calciners and other processes where appropriate.

Bubble substances or parameters

Some competent authorities have considered covering simultaneously all usual main parameters (CO, PM, NO_x, SO₂ and, if present, VOCs) in a bubble approach, with the aim to address site energy consumption and air emissions in a consistent way, and to introduce the same site-level flexibility for all these parameters which are very often interdependent.

In the context of the work undertaken for the revision of this document, SO₂ and NO_x have been recognised as the two parameters which deserve priority in a BREF common methodology for a site-level bubble-expressed AEL calculation, and for which enough supporting information and data have been provided.

Therefore, the methodology developed in Annex 8.6 focuses on SO₂ and NO_x and is based on the available data provided. Nevertheless, extensions to other pollutants (e.g. PM, CO) are not excluded.

Bubble averaging period

The averaging period to be considered will depend on the purpose the bubble tool is used for. In the particular context of this document, the methodology proposed has been based primarily on a yearly average, since a long-term period has been considered the most appropriate for reflecting best performances achievable in normal operating conditions, and giving enough time and flexibility to integrate necessary feedstock, process and fuel adjustments.

However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter term bubble can be derived from the long-term bubble using monitoring results.

Bubble calculation

The site-level bubble is a sum of two terms.

A first term related to the energy system, including at least all furnaces, stand-alone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable AEL concentration ranges expected on each category of installations when BAT is applied. A second term related to the process units including at least a FCC unit if any, and a SRU. This term should be driven by suitable AEL concentrations or specific emission ranges expected on each of them when BAT is applied.

In the context of this document, and for the purpose of expressing meaningful AELs at the site or partial site level, the bubble determination should always be based on concentration and specific emission ranges expected in all concerned installations when BAT is applied, and should involve the following steps:

- Step 1: exhaustive identification and geographical mapping of all included sources;
- Step 2: determination of the off-gas volumetric contributions expected from all included sources;
- Step 3: determination of the mass contributions expected from all included sources;
- Step 4: determination of the bubble-associated monitoring regime.

The actual details of the calculation and necessary information on each of these steps are given in Annex 8.6.

Achieved environmental benefits

By allowing flexibility in how to reduce refinery emissions, the bubble approach puts the focus on environmental benefit (decreasing overall emissions) rather than on individual source compliance.

Examples of how to achieve environmental targets by various reduction means are made available under the following heading.

Environmental performance and operational data

Example 1 is a refinery with a small FCC unit which currently uses 32 % of liquid fuel firing and has a SRU that operates at a recovery efficiency of 98 %. The options considered potentially viable to reduce sulphur emissions are:

- to replace a fraction of the liquid fuel firing with natural gas;
- to use sulphur-reducing additives (SRA) in the FCC unit;
- to install a wet gas scrubber on the FCC unit;
- to upgrade the sulphur recovery tail gas treatment unit which could be to two levels corresponding to the process chosen.

The current total site bubble (SO_2) is $1\,165 \text{ mg/Nm}^3$ (at 3 % O_2), with contributions:

- of 795 mg/Nm^3 from the combustion system;
- $2\,500 \text{ mg/Nm}^3$ from the FCC;
- and $19\,000 \text{ mg/Nm}^3$ from the SRU.

The combustion system contributes 88 % of the flue-gas, the FCC 11 % and the SRU 1 %.

By mass emission, the combustion system contributes 60 %, the FCC 24 % and the SRU 16 % of the total SO₂.

Table 4.63 shows the effect of applying different control options. In this refinery, the base capacity of the SRU is limited and this imposes a maximum use of SRA in the FCC which has to be regenerated. Two degrees of substitution of the liquid fuel are considered to reflect the fact that this is not a commercial fuel and conversion would have to be considered.

Option 1 considers measures on all three sources (Combustion, FCC and SRU) substituting part of the liquid firing, introducing SRA to 30 % removal and upgrading the SRU tail gas unit to a sub-dew point system. The reason for this choice is that the existing unit is a two-bed Claus unit which does not offer an economic advantage to the installation of a SuperClaus unit. This achieves a 31 % reduction in mass emissions.

Option 2 focuses on eliminating liquid firing only. It achieves a 42 % reduction in emissions.

Option 3 focuses on upgrading the SRU tail gas unit to a SCOT plant but achieves only a 16 % reduction in emissions.

Option 4 focuses on scrubbing emissions from the FCC unit and achieves a 21 % reduction in emissions.

Options 5, 6, 7 and 8 consider combined actions based on a full fuel switch to natural gas firing supplemented by actions on the FCC (5), SRU (6, 7) and both FCC and SRU (8). The incremental improvements in mass reduction range from 7 % (5) to 15 % (7) over the fuel switch alone.

Table 4.63: Example of options for SO₂ emissions reduction with site-level management

| % Flue-gas volume | 100 % | 88 % | 11 % | 1 % | Combination |
|--|------------------------------------|----------------------------------|---------------------------|---------------------------|--|
| | Total bubble mg/Nm ³ | Combustion mg/Nm ³ | FCC mg/Nm ³ | SRU mg/Nm ³ | |
| Current situation | 1 165 | 795 | 2 500 | 19 000 | FCC: 32 % liquid fuel firing - SRU 98 % |
| Option 1 | 802 | 583 | 1 750 | 9 700 | Partial fuel switch + FCC SRA 30 % + SRU 99 % |
| Option 2 | 675 | 239 | 2 500 | 19 000 | Full fuel switch |
| Option 3 | 984 | 795 | 2 500 | 990 | SRU 99.9 % |
| Option 4 | 917 | 795 | 250 | 19 000 | FCC scrubber 90 % SO ₂ removal |
| Option 5 | 593 | 239 | 1 750 | 19 000 | Fuel switch and FCC SRA 30 % |
| Option 6 | 582 | 239 | 2 500 | 9 700 | Fuel switch and SRU 99 % |
| Option 7 | 495 | 239 | 2 500 | 990 | Fuel switch and SRU 99.9 % |
| Option 8 | 500 | 239 | 1 750 | 9 700 | SRU 99 % and FCC SRA 30 % and fuel switch |
| NB: Example 1: 32 % oil firing, small size FCC, SRU 98 %. Source: [125, CONCAWE 2011] | | | | | |

Example 2 shows how NO_x control options might be considered. The refinery combustion system comprises many small units ducted to common stacks. The flue-gas temperature at the stacks is too low for SCR to be technically applicable to the combustion system. There are

negligible NO_x emissions from the SRU. In this case, controls on the combustion system comprising a complete switch to gas firing and upgrading the burner system (Option 1) would reduce NO_x emissions by 58 %. Measures on both NO_x sources (Option 3) comprising a partial fuel switch and application of SNCR to the FCC unit would achieve a reduction of 35 %. Measures on the FCC alone (Option 2) are ineffective, resulting in a reduction of 11 %.

Table 4.64: Example of options for NO_x emissions reduction with site-level management

| | Total bubble mg/Nm ³ | Combustion mg/Nm ³ | FCC mg/Nm ³ | |
|--|------------------------------------|----------------------------------|---------------------------|--|
| Current situation | 501 | 492 | 600 | |
| Option 1 | 210 | 161 | 600 | Liquid fuel substitution + LNB |
| Option 2 | 446 | 492 | 100 | FCC SCR 84 % |
| Option 3 | 327 | 332 | 300 | Partial fuel switch + LNB + FCC SNCR (50 %) |
| NB: Example 2: 32 % oil firing, small size FCC. Source: [125, CONCAWE 2011] | | | | |

These two examples show that the several ways to reduce overall emissions from a refinery can differ in their effectiveness.

Cross-media effects

When the optimisation process is only challenged and evaluated through equivalent concentrations set up at the site level rather than at the unit level, it can theoretically lead to possible concern linked to higher emissions at the lower stacks (e.g. SRU). Nevertheless, although all sources are inside the bubble there may be additional constraints on specific source emissions, e.g. from low stacks, to be limited for local air quality requirements.

Technical considerations relevant to applicability

This technique is fully applicable, provided that emitting units and processes are equipped with appropriate continuous monitoring systems, including emissions measurements or process parameters monitoring (see Annex 8.6).

Economics

Monitoring for emissions to a site-specific bubble limit is not different to monitoring for individual sources. It serves two purposes:

- to ensure a better protection for the environment as a whole by being continuously aware of total emissions and enabling to control them;
- and to provide measurement/calculation data to evidence compliance with individual limit values where set.

Monitoring for a bubble requires that all the information needed to assess site-wide emissions is brought together in an automated way, so that an accurate picture is gained. This involves combining different types of information achieved in different ways, e.g. analytical samples, continuous sensor output, discrete measurements with interpolating calculations.

This requires that the site data collection system can assemble this information and generate appropriate management reports at timely intervals, enabling dynamic management. This is very much the same sort of system that should be in place for individual source permitting.

Therefore the extra costs of monitoring for a bubble should be small and related to the generation of formal informational data that can be used for site reporting, alongside the real-time picture of site emissions.

Driving force for implementation

Management and reduction of air emissions and related cost-effectiveness.

Example plants

A number of European refineries have already implemented a full-scale management and monitoring system for the site-level management of emissions of SO₂, NO_x, PM and CO.

Examples of air emission site management of two Belgian refineries are described in the EIPPCB report dated 17/05/2011. The UK approach to define SO₂ air emissions values based on short-term requirements for air quality is illustrated through the EIPPCB report dated 16/11/2011.

Reference literature

[65, COM 2003], [77, REF TWG 2010], [90, COM 2011], [98, COM 2010], [125, CONCAWE 2011], [126, CONCAWE 2011], [127, France 2010].

4.15.6 Anticipation of and adaptation to unfavourable meteorological conditions**Description**

Directive 2008/50/EC on ambient air quality and cleaner air for Europe defines and establishes objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole and also ensures that such information on ambient air quality is made available to the public. In certain unfavourable meteorological conditions, pollutant concentration peaks may be detected in the surroundings of refineries even when they are normally operated and using all expected primary and abatement techniques properly according to their permit. In such conditions, specific measures and tools can turn out to be necessary to anticipate, and further manage and reduce emissions as necessary, in order to guarantee that concentration limit values in the ambient air around the site are being respected.

Two examples of such tools are described in more detail in the Operational data section. They only concern the management of SO₂ emissions.

- The first example, applied by the Total refinery in Donges (France), is based on a daily prediction of the concentrations likely to be reached in most exposed urban areas. A specific dispersion model fitted to the local conditions was developed for this purpose.
- The second example relates to the specific organisation set out for the anticipation of pollution peaks in the surroundings of the ExxonMobil refinery in Notre-Dame-de-Gravenchon (France). This organisation is based on the evolution of real-time ambient concentration measured in several locations distributed according to the directions of the most exposing wind.

In each case, when the tool predicts the likely occurrence of excessive ambient concentrations, appropriate actions are taken at the site level. As a first step, a progressive switch to low-sulphur fuels is required on key energy-consuming units. If needed, a further step consists of a progressive production slowdown or shutdown.

Achieved environmental benefits

A meteorological model-based system has been implemented for the Donges refinery since the end of 2006. Between 2007 and 2008, five meteorological episodes with SO₂ ambient air concentrations over the limit values were reported, compared to 28 episodes recorded between 2002 and 2005.

Environmental performance and operational data

In the case of Donges

The system is predictive and follows the steps illustrated in the local weather forecast handled as a minimum on a daily basis, using a dedicated software that actually adjusts and refines by physical calculation the spot meteorological conditions in particular areas of interest. The model has been initially configured with local historical and physical data. Concentrations are predicted by dispersion modelling based on these calculated meteorological conditions, where all main emission contributing sources are physically described and separately addressed. The results are used by the scheduling department of the refinery for daily adjustment of the operational planning.

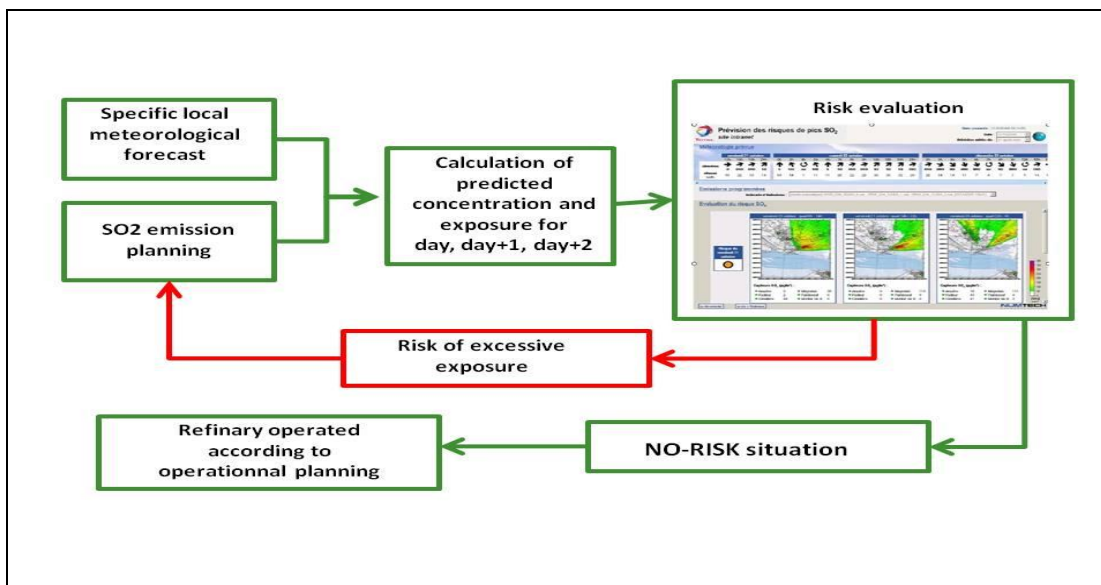


Figure 4.45: Flowchart of an emission management system for anticipating unfavourable meteorological conditions - Example of Total refinery in Donges

In the case of Rouen

The system is reactive and based on an existing network of 15 permanent multi-parameter automatic measuring devices settled all over the Rouen urban and industrial harbour area, and is handled and maintained by a local air-monitoring non-profit organisation. Two of these measuring devices have been selected due to their geographical location, the results of them being processed according to the two following procedures as displayed in Figure 4.46.

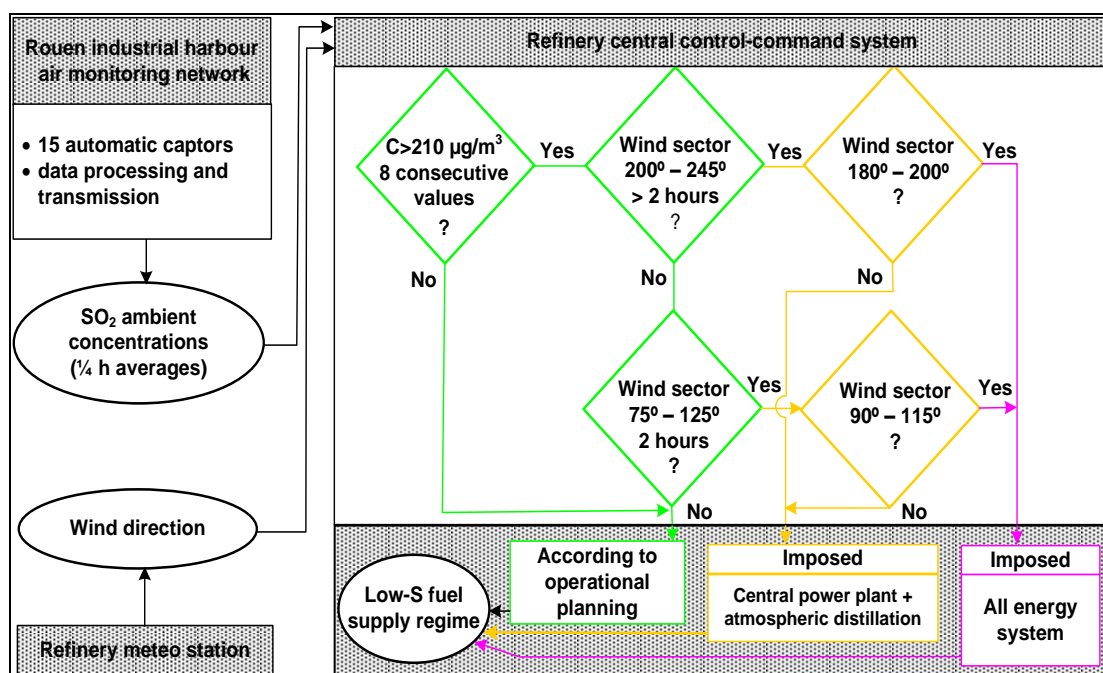


Figure 4.46: Flowchart of an emission management system for anticipating unfavourable meteorological conditions - Esso refinery in Notre-Dame-de-Gravenchon

Cross-media effects

No data submitted.

Technical considerations relevant to applicability

Systems based on local modelling require the existence of public or private meteorological services which are able to provide the necessary forecast data on a continuous basis. The applicability of systems based on a continuous measuring of ambient air concentrations in urban target areas is significantly facilitated when they can rely upon an existing air quality monitoring organisation which already operates and maintains a network of appropriate sensors.

Economics

In the case of Donges, the initial investment for the system development and basic configuration was around EUR 0.45 million (2006). The annual operating costs are evaluated at EUR 0.1 million/yr, covering software and hardware maintenance, as well as the acquisition of daily meteorological forecasts at the appropriate frequencies and geographical scales for providing, as necessary, calculation starting conditions to the system. As such, the measures actually taken for the SO₂ reduction itself during concerned meteorological episodes are highly variable by year. They were in the range of EUR 1 – 6 million per year in 2006, 2007 and 2009.

Driving force for implementation

Prevention or limitation of potential exposure to ambient air concentrations over limit values, by anticipation or early detection of unfavourable meteorological episodes, in order to prevent and reduce health and environmental impacts.

Example plants

A number of both kinds of systems are implemented by refineries in France (see above). In Italy, similar systems have existed for more than 15 years in the province of Syracuse (East Sicily) a densely populated area with four refineries, and several chemical and power plants. The system works with a permanent monitoring network of 24 fixed stations (SO_x, NO_x, PM, VOC, benzene, etc.) It includes a permanent meteorological station equipped to predict the thermal inversion conditions and worsening of the air quality. In the south of Spain, the Cepsa La Rabida Refinery uses a model taking into account real-time and meteorological data.

Reference literature

[39, French contribution to TWG (item 4) 2009].

4.16 Isomerisation

4.16.1 Active chloride-promoted catalyst isomerisation process

Description

More information can be found in Section 2.16.

Achieved environmental benefits

Higher process efficiencies compared with the zeolitic catalysts and lower reaction temperatures (less energy consumed).

Cross-media effects

The chloride-promoted, chlorinated alumina catalyst (containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activities. This is converted to hydrogen chloride in the reactor. The chloride-promoted catalyst cannot be regenerated.

Operational data

The highly active chloride-promoted catalyst and the chlorinated alumina catalyst (containing platinum) operate at a relatively low temperature (150 – 175 °C and 20 barg) and give the highest octane improvement. In such a reactor, the feed must be free of oxygen and sulphur sources, including water to avoid deactivation and corrosion problems. The oxygen deactivation is not reversible, nevertheless the sulphur can be desorbed from the catalyst surface. This desorption process of sulphur species from the catalyst consumes utilities and energy.

Applicability

This catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to 0.5 ppm is required.

Economics

Investment estimated (based on ISBL, US Gulf Coast 1998): EUR 4 150 – 10 400 per m³/d.

The investment for installation (based on: 2nd quarter 1998 US Gulf Coast) was evaluated for 1 590 m³/d of fresh feed capacity at EUR 8.8 million (±50 %).

Driving force for implementation

Production process.

Reference literature

[183, HP 1998], [228, TWG 2000].

4.16.2 Zeolitic isomerisation process

Description

More information is given in Section 2.16. Some refiners need more octane from the light straight-run naphtha fraction than is possible from the O-T zeolitic isomerisation process. Adsorption technology can then be used to remove the unconverted normal paraffins. The utilities needs for that process are quite low.

Achieved environmental benefits

No chloride compounds are used in these types of processes. The zeolite and sulphated zirconia catalyst can be regenerated several times before sending the catalyst to a reclaimer to recover the platinum.

Cross-media effects

Higher temperature of the process, requiring more heating.

Operational data

The zeolite catalyst operates at significantly higher temperatures (250 – 275°C and 28 barg) and is much more tolerant to contaminants, though the resulting octane improvement is lower.

Applicability

The zeolite catalyst is mainly used for non-hydrotreated feed streams. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures.

Refiners with idle hydroprocessing equipment, such as old catalytic reformers or hydrodesulphurisation units, can consider converting this equipment to the once-through zeolitic isomerisation process. With isomerisation, a 10 to 12 octane number increase for the C₅ - 71 °C light naphtha can be achieved.

Economics

The estimated cost of the reaction process is EUR 4 654 per m³/d. For the absorption process, the investment is EUR 18 900 – 25 160 per m³/d. The catalyst and adsorbent cost is around EUR 1 700 per m³/d.

Driving force for implementation

Production process. Selection of a once-through or recycle scheme depends on factors such as quantity of light naphtha to be blended in the gasoline pool, the required octane number of the gasoline pool and the availability of other high-octane gasoline blend components. If the isomerate product has an octane number exceeding 87, a recycle scheme is the only option. Selection of a fractionation-based scheme or an absorption-based scheme is dependent on feed composition and to a certain extent on the product requirements. In general, it can be said that the fractionation-based scheme is lower in investment but significantly higher in operating costs as a result of high energy requirements.

Reference literature

[175, Meyers 1997], [183, HP 1998], [228, TWG 2000].

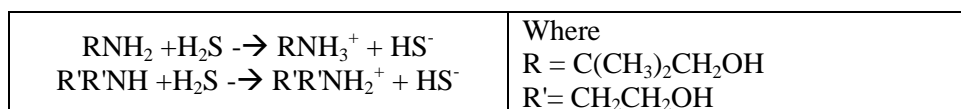
4.17 Natural gas plants

As mentioned in the Scope and in Section 2.17, the processes dealt with in this section are those used in the refining of natural gas. As with mineral oil refineries, the processes used on production platforms are not included in this BREF.

4.17.1 Amine sweetening of natural gas

Description

Many reactions may take place in the process where H₂S is absorbed into an aqueous blended amine solution, mainly by proton transfer as given below.



Technical description

The process is illustrated in Figure 4.52 of Section 4.23.5.1.

If the recovered H₂S gas stream is not to be used as a feedstock for commercial applications, the gas is usually passed to a tail gas incinerator in which the H₂S is oxidised to SO₂ and is then released to the atmosphere via a stack. More information can be found in Section 4.23.5.1.

Achieved environmental benefits

Reduction of H₂S concentration in natural gas.

Environmental performance and operational data

See Section 3.17

Cross-media effects

See Section 4.23.5.1.

Operational data

The recovered hydrogen sulphide gas stream may be:

- vented,
- flared in waste gas flares or modern smokeless flares,
- incinerated, or
- used for the production of elemental sulphur or sulphuric acid.

Technical considerations relevant to applicability

Fully applicable.

Economics

See Section 4.23.5.1.

Driving force for implementation

To comply with sulphur specifications of natural gas.

Example plants

At present, the amine process (also known as the Girdler process) is the most widely used method for H₂S removal.

Reference literature

[99, Mandal et al.2005], [172, MRI 1997], [173, HMIP UK 1997].

4.17.2 Sulphur recovery unit

Extensive information can be found in Section 4.23.5.2.

4.17.3 Techniques to reduce VOC emissions

During the routine operation of natural gas terminals and other processes, it is necessary to prevent releases to air of natural gas. Techniques to consider to reduce these emissions are given below:

- minimise the frequency of sphere pigs use by operating sealines at a high velocity, i.e. use 'mist flow' conditions;
- minimise the recovery of spheres by use of receivers holding several devices;
- use vent receivers of high-pressure gas to a low-pressure part of the process for gas recovery by recompression, before opening for access to sphere pigs;
- minimise the occasional shutdown and venting of process plant (when necessary, e.g. for maintenance, upset and changeover purposes) by appropriate plant selection and design;
- avoid the use of refrigerants for gas dew point control that are of significant environmental concern (CFCs);
- condense and incinerate overheads and any gas vented from storage and glycol and methanol regeneration units;
- apply leak detection and repair (LDAR) programme (see Section 4.23.6.1);
- maintain VOC emissions, including fugitives, within a range of 200 – 250 kg/h (300 – 350 kg/MNm³).

Reference literature

[173, HMIP UK 1997], [207, TWG 2001].

4.17.4 Techniques to reduce NO_x emissions

NO_x emissions come from the combustion processes applied in the natural gas plant. The techniques that can be applied for the control and abatement of NO_x are the same as those applied to refinery fuel gas. See Sections 4.10.4 and 4.23.3 for a detailed explanation.

4.17.5 Techniques to reduce water emissions

Description

Prevention techniques that may be applied to reduce the releases to water can be:

- minimise and control, if possible, the quantity and contamination level of waste water to be treated onshore 'at source', i.e. waste water coming from offshore activities;
- use of a three-phase separator on the liquids from the slug catcher to control and minimise the hydrocarbon content of the aqueous phase;
- treat sour water in a sour water stripper unit (see Section 4.24.2);
- keep process effluent from glycol or methanol regeneration plants and any other high-BOD/COD effluents separate from other streams, e.g. surface water, and treat before discharge to the site effluent system;
- apply water management techniques (see Section 4.15.4).

The techniques that may be used in the waste water treatment are described in Section 4.24.

Achieved environmental benefits

The achievable emission levels for well-performing waste water treatment plants within a natural gas plant are shown in Table 4.65.

Table 4.65: Typical WWTP performance in natural gas plants

| Water parameter/compound | Concentration (ppm) | Load (kg/MNm³ feedstock) |
|--|----------------------------|--|
| Waste water | | 160 m ³ /MNm ³ |
| Total oil content | 0.1 – 5 | 0.4 – 0.6 |
| TOC | 60 – 100 | 3.5 – 12 |
| COD | 400 | |
| Suspended solids | 25 | |
| Phenol | 0.1 - 0.5 | |
| NB: Values in this table are daily averages. | | |

Reference literature

[77, REF TWG 2010], [173, HMIP UK 1997], [207, TWG 2001].

4.17.6 Techniques to reduce waste generation**Description**

Techniques that may be applied to reduce waste generation are:

- Returning catalysts, absorbents, adsorbents, etc. to the manufacturers for recycling.
- Desalination of the glycol purge stream, which will give rise to solids for disposal, and ensuring any residual glycol should first be reduced to a low level.
- Some of the gas fields contain mercury vapour in very low concentrations. This mercury is removed from the gas in a ‘cold trap’ (e.g. by gas expansion) and recovered as a mercury-containing sludge. A specialised company processes this sludge by treatment in a vacuum distillation unit.

Reference literature

[173, HMIP UK 1997], [207, TWG 2001].

4.18 Polymerisation

4.18.1 Reduction of emissions and use of catalyst within the process

Description

More information is given in Section 2.18.

Achieved environmental benefits

Reduction of the process emissions and reduction of acid consumption and consequently waste. Good polymerisation units can reduce the phosphoric acid consumption to levels of 0.1 – 0.2 g/t of polymer produced. Another source relates that the typical catalyst consumption (H_3PO_4 + support) is around 1.18 kg catalyst per tonne of polymer produced.

Cross-media effects

No cross-media effects.

Operational data

Available data is provided in Table 4.66.

Table 4.66: Typical utility consumption of a polymerisation plant

| Utilities | |
|---|-----------|
| Electric power (kW/tonne of C_5+ product) | 20 – 28 |
| Steam (t/tonne of C_5+ product) | 0.7 – 1.1 |
| Cooling (m^3 /tonne of C_5+ product) | 4.4 – 6.0 |

Applicability

Commonly used as a production process.

Economics

The catalytic condensation process is relatively simple to operate and requires minimum labour. Its simplicity is reflected in the operating requirements summarised in Table 4.67.

Table 4.67: Typical operating costs of a catalytic condensation process

| | |
|---|-------------------|
| Catalyst and chemical cost (EUR/tonne of C_5+ product) | 5.00 – 8.20 |
| Labour and operating cost (workforce) | 1 operator-helper |
| Typical operating cost (EUR/t C_5+ product) | 20 – 30 |
| Investment (EUR1 995/(t/yr) of C_5+ product) | 50 – 95 |

Only one operator is required. Overall, the cost of operating a catalytic condensation unit ranges from EUR 16 to EUR 22.6 per m^3 of C_5+ polymer gasoline. This cost includes utilities, labour, catalyst, chemicals, and an allowance for the process royalty, but does not include any direct or indirect capital-related costs.

Driving force for implementation

Production process.

Example plants

Some polymerisation processes are running in European refineries. Nowadays alkylation units are more predominant than polymerisation units, even though polymerisation units are cheaper.

Reference literature

[175, Meyers 1997], [183, HP 1998], [207, TWG 2001].

4.18.2 Management and reuse of the catalyst

Description

Two techniques can be applied to minimise the impact of catalyst disposal.

- The catalyst to be disposed of from the process is potentially pyrophoric and requires special treatment. However, removal by steam/water prevents any risk of fire. The catalyst solidifies in situ, and removal is achieved manually under nitrogen purge, or more recently by 'explosive' steam decompression with steam suppression to a catchment system. The catalyst may then be sent either for off-site disposal as special waste or to on-site treatment. On-site treatment involves neutralisation and fixing with cement. The material may then not be classified as special waste.
- The spent catalyst can be reused as fertiliser or as phosphorous feed to the biotreater.

Achieved environmental benefits

Reduction of risk of fire due to the pyrophoric characteristics of the catalysts and reduction of waste generation.

Cross-media effects

No cross-media effects.

Operational data

Disposal frequencies of up to 12 times per year may be expected.

Applicability

Fully applicable.

Driving force for implementation

Treatment of catalyst and reuse of phosphorous compounds within the refinery.

Example plants

No detailed data.

Reference literature

[149, Ministero dell'Ambiente 1999].

4.19 Primary distillation units

As mentioned in Section 3.19, the atmospheric and vacuum distillation units are large consumers of heat. The techniques to consider for application to the crude oil furnaces are those described in the section dealing with the energy system (Section 4.10).

4.19.1 Progressive distillation unit

Description

A progressive distillation unit with integrated CDU/HVU, which saves up to 30 % on total energy consumption for these units. The technique includes atmospheric distillation (topping), vacuum distillation, gasoline fractionation, a naphtha stabiliser if required and a gas plant.

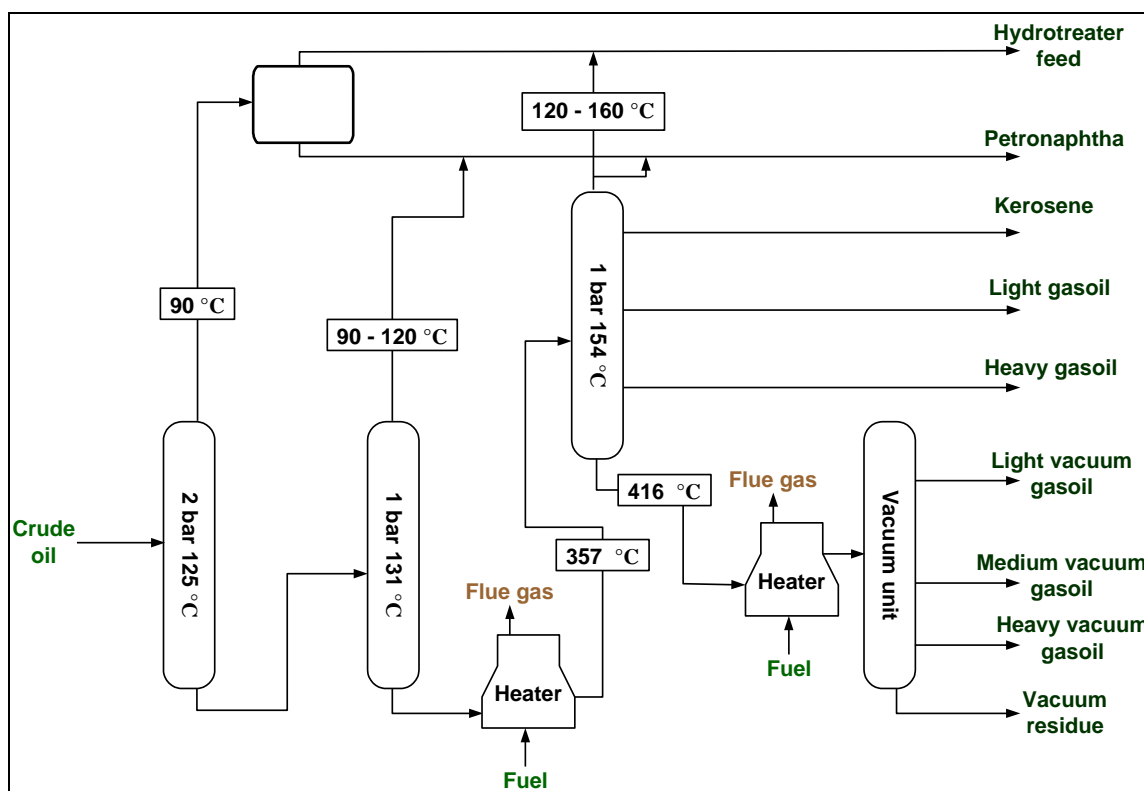


Figure 4.47: Process flow diagram of a progressive distillation unit

Achieved environmental benefits

The heater process duty (MWh/100 tonnes of crude) of a distillation capacity of 10 million tonnes per year is around 17.3 for an Arabian light crude. Using progressive crude distillation it is reduced to 10.1. The specific energy consumption (overall energy consumption in tonnes of fuel equivalent per 100 tonnes of crude) for a distillation capacity of 10 million tonnes per year is 1.7–2.0 for an Arabian light crude, whereas using the progressive distillation unit only consumes 1.15. The energy savings for a 9 700 000 tonnes/yr refinery is in the range of 50 000 tonnes of heavy fuel compared to conventional techniques.

Total primary energy consumption

For Arabian light or Russian export blend: 1.25 tonnes of fuel per 100 tonnes of crude.

For Arabian heavy: 1.15 tonnes of fuel per 100 tonnes of crude.

Progressive distillation is the extreme of heat integration between atmospheric and vacuum distillation. It also prevents the superheating of light cuts to temperatures higher than strictly

necessary for their separation and it prevents degrading the thermal levels associated with the drawing-off of heavy cuts.

Cross-media effects

No cross-media effects identified.

Environmental performance and operational data

Table 4.68: Energy consumption of the progressive crude distillation when the same plant is used to process two types of crude oil

| | Heavy Arabian (887 kg/m ³) 6.5 Mt/yr | | | Ekofisk (810 kg/m ³) 5 Mt/yr | | |
|---|---|-------------|-------------|---|-------------|-------------|
| | Consumption | TOE/h | TOE/100 t | Consumption | TOE/h | TOE/100 t |
| Fuel (MWh/h) | 67.5 | 5.81 | 0.75 | 67.5 | 5.81 | 1.04 |
| Steam (tonnes/h) | 15.95 | 0.8 | 0.11 | 21.0 | 1.05 | 0.19 |
| Electricity (MWh/h) | 6.4 | 1.41 | 0.18 | 6.4 | 1.41 | 0.25 |
| TOTAL | | 8.02 | 1.04 | | 0.27 | 1.48 |
| NB: The energy consumption is defined according to the following hypothesis: TOE (tonne of oil equivalent) = 11.6 MWh. kg of low-pressure steam = 0.581 kWh. Yield of the electrical power plant = 39 %. Products are sent to storage (cold temperature). | | | | | | |

Table 4.69: Typical utility requirements per tonne of crude feed in the US

| Typical utility requirements per tonne of crude feed | | Units |
|---|-----------|----------------|
| Fuel fired | 107 – 140 | kWh |
| Power | 6.6 – 8.8 | kWh |
| Steam, 4.5 barg | 0 – 17 | kg |
| Water cooling ($\Delta T = 15\text{ }^{\circ}\text{C}$) | 1.4 – 2.8 | m ³ |
| NB: Data converted using average value of 1 tonne for 7.3 barrels of crude oil. | | |

Technical considerations relevant to applicability

The process is applicable to all or part of these units when being constructed and can also be used in revamps for debottlenecking. It includes, for example, adding a preflash column to reduce the fuel consumption.

Economics

Reduced fuel consumption can be achieved and thus reduced operating costs of the distillation units.

Investment (based on 11.45 Mt/yr including atmospheric and vacuum distillation, gas plant and rectification tower): EUR 41 000 – 55 000 per t/yr (US Gulf Coast 1998).

Driving force for implementation

To reduce fuel consumption in refineries.

Example plant(s)

Some European refineries employ a progressive distillation unit with an integrated CDU/HVU.

Reference literature

[177, WRA 1999], [183, HP 1998], [191, UBA Austria 1998].

4.19.2 Heat integration of crude distillation units

Description

There is a tendency towards improved heat integration with crude and other units. The high energy consumption of the CDU makes heat integration very relevant. To optimise heat recovery from the atmospheric distillation column, two or three reflux streams are normally kept in continuous circulation at several points per top and middle pumparounds. In modern designs, integration with the high vacuum unit and sometimes the thermal cracker is achieved. Some techniques applied are given below.

- Optimise the heat recovery, studying and implementing the optimal energy integration. In this context, major progress has been made in recent years in understanding the design of efficient heat recovery networks. Pinch analysis has emerged as a tool for the evaluation of total systems designs, helping to balance investments against energy savings.
- Apply pinch analysis to the crude preheat train heat integration. Increase crude preheat temperature and minimise heat losses to air and cooling water.
- Increase crude distillation column pumparounds from two to four. Reboil sidestrippers with a heat transfer oil rather than by steam stripping.
- Heat transfer in the crude preheating can be improved using specific antifouling treatments in the crude heat exchanger train. Antifoulants are available from many chemical companies and, in many applications, are efficient in increasing the run cycle length of the exchangers; an antifoulant can help prevent the plugging of tube exchangers, improving heat recovery and preventing hydraulic losses, depending on the nature of the fouling. Service factors of the various units/trains, as well as heat recovery (energy efficiency) increase at the same time.
- The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits

Reduced fuel consumption in distillation columns.

Cross-media effects

In the case of highly heat-integrated units, the refinery complex as a whole becomes more susceptible to unstable conditions arising in an individual unit.

Applicability

Integration in retrofitting applications will normally depend on the plot space available and the possibility to execute these modifications in the available shutdown time. Except in a very few cases, this technique is commonly applicable.

Driving force for implementation

Reduced energy consumption and the associated CO₂ emissions within the refinery.

Example plants

Heat integration procedures are extensively applied in crude units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature

[155, API 1993], [174, HMIP UK 1995], [221, Italy 2000].

4.19.3 Heat integration of the vacuum distillation units

Description

The number of side-streams in a high vacuum unit is chosen to maximise heat integration for producing streams at different temperatures, rather than to match the number of products required, with the exception of the lube oil vacuum distillation units. Heat integration with the

crude units can be achieved. The atmospheric residue is then taken directly from the crude distillation unit to the vacuum furnace, and the product streams and circulating refluxes of the high vacuum unit are cooled against the crude oil.

The main feed stream to the high vacuum unit is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue, which is either supplied directly hot or (relatively) cold from storage tanks. The latter option requires higher energy consumption.

The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits

Reduction of fuel consumption in the refinery.

Cross-media effects

In the case of highly heat-integrated units, the refinery complex as a whole becomes more susceptible to unstable conditions arising in an individual unit.

Applicability

Integration in retrofitting applications will normally depend on the plot space available and the possibility to execute these modifications in the available shutdown time. Except in a very few cases, this technique is commonly applicable.

Driving force for implementation

To reduce fuel consumption and the associated CO₂ emissions within the refinery.

Example plants

Heat integration procedures are extensively applied in vacuum units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature

[174, HMIP UK 1995], [155, API 1993], [221, Italy 2000].

4.19.4 Use of vacuum pumps and surface condensers

Description

This technique consists of the use of vacuum liquid ring compressors instead of steam ejectors.

Achieved environmental benefits

Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily waste water stream. Replacing the steam ejectors by vacuum pumps will reduce the sour water flow from 10 m³/h to 2 m³/h. The vacuum may be generated by a combination of vacuum pumps and ejectors to optimise energy efficiency. Other benefits are linked with cross-media effects.

Cross-media effects

Replacement of the steam ejectors by vacuum pumps will increase the electricity consumption for vacuum generation, but will reduce the heat consumption, the cooling water consumption, the electricity consumed for cooling pumps and the consumption of agents used for the conditioning of cooling water. Within the refinery, there are many processes where surplus steam can be recovered and used for the production of vacuum. However, an energy management analysis will help to decide whether the use of surplus steam for steam ejection instead of applying vacuum pumps is more efficient than using surplus steam for other purposes. The reliability of both systems is also to be taken into account, as usually steam ejectors are more reliable than vacuum pumps.

Operational data

The use of vacuum pumps consumes electricity.

Applicability

May not be applicable in retrofit cases. For new units, vacuum pumps either in or not in combination with steam ejectors to achieve a high vacuum (10 mm Hg) are needed, as well as a spare in case the vacuum pump fails.

Driving force for implementation

To reduce the production of waste water.

Example plants

At present, vacuum pumps are used more often than ejector sets.

Reference literature

[155, API 1993], [207, TWG 2001].

4.19.5 Reduction of the vacuum pressure in the vacuum distillation unit

Description

Lowering the vacuum pressure, e.g. down to 20 – 25 mm Hg, will allow a reduction in the furnace outlet temperature, while maintaining the same target cut point of the vacuum residue.

Achieved environmental benefits

This technique would provide some benefits, both in terms of energy conservation and pollution reduction. The environmental benefits are:

- a lowered potential for cracking or coking at furnace tubes;
- a reduced cracking of feed to lighter products;
- a lowered furnace fired duty and hence lowered fuel consumption.

Cross-media effects

Energy (electricity or steam) is necessary to generate the vacuum.

Applicability

Applicability is usually limited by the tower capacity, the condensing fluid temperature, or other material restrictions.

Driving force for implementation

Reduce the heat duty of the vacuum distillation process.

Reference literature

[155, API 1993], [221, Italy 2000].

4.19.6 Treatment of non-condensables from the vacuum ejector set condenser

Description

These techniques to control releases from vacuum units include processes such as amine scrubbing (see Section 4.23.5.1), compression into refinery fuel gas and burning in adjacent process furnaces, or combinations thereof. The gases from some units may contain significant amounts of air and such gases are normally best combusted locally. Amine scrubbing techniques may need to be applied carefully, as hydrocarbon contamination could cause foaming problems in amine regeneration units.

Non-condensables from overhead condensers can be passed to light ends treatment or recovery systems or refinery fuel gas systems; sour incondensable gases vented from sealed barometric pumps of vacuum distillation units should be extracted and dealt with in a manner appropriate to the nature of the sour gas.

This is a control technique applicable to the non-condensable emissions vented from the vacuum ejectors or pumps, consisting of venting into blowdown systems or refinery fuel gas systems and incineration in furnaces or waste heat boilers.

Achieved environmental benefits

Vacuum distillation column condensers may emit 0.14 kg/m³ of vacuum feed and can be reduced to negligible levels if they are vented to the heater or incinerator. Pollution reduction is achieved if vacuum gaseous streams (vent gas) are routed to an appropriate amine scrubbing unit instead of being directly burnt in the process heater. Vacuum vent gas routing to scrubbing requires significant investment due to compressor costs.

The efficiency of incineration control techniques is generally greater than 99 % as regards NMVOC emissions.

Cross-media effects

In the incineration technique, the combustion products have to be accounted for.

Reuse of waste water generated by the overhead reflux drum might have an effect on the desalter pH and the desalted yield of some components.

Applicability

Fully applicable.

Operational data

Questionnaire 15 reports that the non-condensable streams from vacuum distillation, currently routed to a furnace, typically involve a small flow rate with a high concentration of H₂S. It is estimated to represent close to 15 % of the total sulphur refinery emissions. A project is ongoing for treating these streams through an amine unit to therefore reduce these emissions. Similar projects are reported for other refinery sites.

Driving force for implementation

To reduce the emissions of pollutants, for example in the context of a 'bubble' approach.

Example plants

Applied in some European refineries.

Reference literature

[171, UN/ECE 1998], [172, MRI 1997], [Questionnaire 15].

4.19.7 Waste water treatment and reuse

Description

This topic is also discussed in Section 4.15.4. Techniques to consider are the following:

- Reuse of waste water generated by the overhead reflux drum. This water can be reused as a desalter wash water.
- Passing sour water from atmospheric and vacuum unit condensates to a stripper in enclosed systems.
- Optimising water reuse by application of side-stream softening to blowdown streams.

Achieved environmental benefits

Reduction of water consumption and reabsorption pollutants.

Applicability

Fully applicable.

Driving force for implementation

Reduce water consumption.

Reference literature

[155, API 1993].

4.19.8 Other techniques to consider in the atmospheric units

Description

Some other techniques to consider are given below.

- Where applied, ammonia injection should be handled in enclosed systems. Alternative neutralising techniques are available and can reduce the ammonia/ammonium load on sour water and sulphur recovery systems.
- Decoking vents need to be provided with suitable knockout and dust suppression facilities; suitable methods for preventing emissions during clean-out procedures need to be used.
- Many oily sludges can be sent to crude distillation (or an alternative to the coking unit, see Section 4.7.5) where they become part of the refinery products. This technique typically implies sending the light slops to floating roof tanks (double sealed), and the heavy slops typically to fixed roof tanks. Typically the heavy slop, after settling, is blended with liquid fuel. The blended light slops, after enough settling, may also be blended with liquid fuel or sent to the crude distillation at a mixing rate to avoid fouling.
- Pressure relief valves on column overheads; relief from overhead accumulator should be piped to flare, as should the vent points.
- Use of spent caustic instead of fresh caustic for corrosion control on distillation unit. (for more information see Section 4.20.2).
- New additives (amines) can substitute caustic for corrosion control.
- Special additives (thiophosphates) can be used for treating naphthenic crudes.
- Online cleaning (wet or dry) of heater convection sections.
- Floating pressure control: operating the column at the minimum possible pressure minimises the energy cost of separation and improves tray efficiencies and latent heating from vaporisation. The disadvantage is that the operating temperature is no longer an indication of composition.

Operational data

The processing of oily sludges in the crude distillation may generate problems in the desalter or may foul up the heat exchangers of the distillation column.

Reference literature

[155, API 1993], [207, TWG 2001].

4.20 Product treatments

A brief explanation on which kind of processes are included within this section is given in Section 2.20 and within the Scope.

4.20.1 Cascading of caustic solutions

Description

An overall reduction in the caustic consumption of wet treating units can be achieved if semi-spent caustic from one treating unit can be reused in another one. A typical example of this procedure is the use of the bleed of regenerated caustic (e.g. in mercaptan treaters for catcracked gasoline or for the removal of H₂S or thiophenols) in a prewash step of the non-catalysed cat cracked gasoline sweetening processes. An example of a caustic integration scheme is given in Figure 2.31.

Achieved environmental benefits

Reduction of the use of caustic solutions.

Operational data

Systems handling spent caustic require particular care regarding sulphur compounds.

Economics

Table 4.70: Data on costs associated with various gasoline and distillate sweetening processes

| Product | Types of gasoline sweetening processes | Estimate capital cost, EUR million | Est. operating cost, EUR/m ³ |
|----------------------------|--|------------------------------------|---|
| LPG | Extraction ⁽¹⁾ | 2.2 | 0.05 |
| Light naphtha | Minalk | 1.1 | 0.04 |
| | Caustic-free | 1.1 | 0.15 |
| Heavy naphtha and kerosene | Conventional fixed bed | 2.6 | 0.18 |
| | Caustic-free | 2.6 | 0.40 |

⁽¹⁾ Include pretreating and post-treating facilities.
 Sample economics of the MEROX process on the basis of 1 590 m³ per stream day capacity for various applications. The capital costs are for modular design, fabrication and erection of MEROX plants. The estimated modular cost is inside battery limits, US Gulf Coast, FOB point of manufacturer. The estimated operating costs include catalysts, chemicals, utilities and labour.

Sweetening treatment is much cheaper than hydrotreating, both in terms of capital investment and operational costs. The caustic is normally almost fully regenerated and only a small bleed results.

Reference literature

[158, CONCAWE 1990], [166, CONCAWE 1999], [175, Meyers 1997].

4.20.2 Management of the spent caustic

Description

Caustics are used to absorb and remove hydrogen sulphide, mercaptans and phenol contaminants from intermediate and final product streams. Spent caustic solutions from some sweetening units are odorous and need to be handled in enclosed systems and treated as necessary before release at a controlled rate to the effluent system. Several techniques exist to maximise the reuse of caustics within a refinery. They include recycling within the refinery or outside the refinery or destruction within incinerators.

Techniques to consider are:

- Neutralisation and stripping.
- Incineration which can be an appropriate alternative to waste water treatment because of the very high concentration of cresylics, naphthenes, mercaptans and other organic compounds in spent caustic solutions (COD \gg 50 g/l).
- Handling and disposal of dry spent caustic in a manner that prevents dust generation. It should not be disposed of to the land.
- Reuse of spent caustic within the refinery.
- Corrosion control on crude distillation units using spent caustic rather than fresh caustic. Unstable chloridric (magnesium) salts that are not extracted from the crude oil in the desalter will decompose upon heating into the crude distiller and cause chloridric corrosion. To prevent corrosion of the exposed equipment, small quantities of caustic (sodium) are injected in the crude oil feed by which the chloridric components are neutralised due to the formation of stable sodium chloride. For the purpose of the neutralisation of chloridric decomposition products, often spent caustic can be used, which is recommended as well to minimise waste generation.
- Recycling to downstream of the crude desalter or sour water strippers.
- Addition to biotreaters for pH control.
- Recycling caustics containing phenols on site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation. The caustic can then be treated in the refinery waste water system.
- Reusing spent caustic (generally classified into: sulphidic, cresylic and naphthenic) outside the refinery:
 - In paper mills (sulphidic caustic only).
 - As raw material for Na₂SO₃ (may require segregation of various caustics).
 - In chemical recovery companies if concentrations of phenol or hydrogen sulphide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical.
- Regenerating or oxidising spent caustic by:
 - treatment with hydrogen peroxide;
 - fixed bed catalyst;
 - pressurised air: 120 – 320°C; 1.4 – 20.4 MPa;
 - biological system.

Achieved environmental benefits

Reduction of odour emissions and caustic use.

Cross-media effects

The cross-media effects found in the different techniques mentioned above are given below.

- The presence of caustic within the crude unit may enhance the coke formation within downstream units.
- The increase of phenols and BTX loads to waste water treatment. As a consequence, the degradation efficiency of the biotreater can be adversely affected or the emissions from the waste water treatment plant for these components can increase. Mercaptans, cresyls, and naphthenes can have an adverse impact on the biotreatment system.

Operational data

Systems handling spent caustic require particular care regarding sulphur compounds.

Driving force for implementation

To reduce caustic use.

Example plants

A number of refineries are able to regenerate their spent caustic, but others have to dispose of some excess quantities, mainly from caustic prewash activities. Usually these quantities are small and can be managed within their effluent treatment system or, if this is not the case, they are disposed of via contractors for use as a bleaching agent in the paper and pulp industry. Some refineries sell their concentrated phenolic caustic for the recovery of cresylic acids. Some refineries work up the phenolic caustics themselves. From the extraction process, the disulphide recovered can be sold as product, or be recycled to a hydrometer or incinerator.

Reference literature

[166, CONCAWE 1999], [202, Dekkers 2000], [207, TWG 2001].

4.20.3 Incineration of foul air vented from sweetening

Description

Foul air vented from sweetening processes contains sulphur compounds that typically have a strong odour. The range of quantity of sulphur in the foul air vented from the sweetening processes is around 0.7 – 7 kg/day (disulphide concentration can be as high as 400 ppm) for a 10 000 t/d crude unit and the percentage contribution it makes to the stack gases where it is incinerated has been estimated at 0.16 – 2.48 %. For this reason, the abatement prior to incineration is not justified and the foul air vented from sweetening processes is incinerated in local furnaces.

Reference literature

[207, TWG 2001].

4.20.4 Replace clay filtration with hydrotreating

Description

Where a need to remove colour bodies and olefins exists, hydrotreating replaces clay filtration as the method of choice. Hydrotreating does a better job of improving colour and increasing stability against oxidation, and has no yield loss (the oil measured in the spent filter clay represents a loss of some of the most valuable products produced in a refinery). It also eliminates the problem of spent clay disposal.

Achieved environmental benefits

Reduction of waste generation.

Cross-media effects

Need for hydrogen and energy consumption. See Section 4.10.2.3.

Operational data

See Section 4.10.2.3

Economics

See Section 4.10.2.3.

Driving force for implementation

Product requirements.

Reference literature

[164, Noyes 1993].

4.20.5 Catalytic dewaxing

Description

The removal of wax is necessary to produce lubricating oil which meets desired low temperature properties. Many processes require solvent, chilling and filtration stages for separation.

Catalytic dewaxing processes, based on selective molecular sieve-based catalyst, typically produce a lower-pour product than solvent dewaxing. This system produces fuel components instead of waxes. A short description of the technique can be found in Section 2.20.

Achieved environmental benefits

The foul odours and the sulphur content of the products produced with this technique are lower than with solvent dewaxing. The products generated by the cracking of the wax remain as part of the product.

Cross-media effects

Hydrogen consumption, typically 20 – 62 m³/tonne feed (100 – 300 scf/bbl).

Applicability

Fully applicable for new units. Catalytic dewaxing is unlikely to be retrofitted on another type of dewaxing process because it is a completely different process. Catalytic dewaxing has a pour point advantage, but has a viscosity index disadvantage compared to solvent dewaxing.

Economics

Table 4.71 compares the relative cost of debottlenecking a 300 kt/yr solvent extraction complex to 500 kt/yr with the cost involved in the construction of a new 200 kt/yr solvent extraction complex and hybrid debottlenecking with catalytic dewaxing.

Table 4.71: Cost data for a 200 kt solvent extraction dewaxing unit

| Cost parameters | New solvent extraction (200 kt/yr) (% of the total cost) | Hybrid debottlenecking (from 300 to 500 kt/yr) (% of the solvent extraction cost) |
|--|---|---|
| Capital change | 36 | 24 – 36 |
| Fixed costs | 20 | 7 – 9 |
| Variable costs | 8 | 8 |
| Hydrocarbon cost | 35 | 11 |
| Total | 100 | 50 – 64 |
| NB: Investment based on: 795 m ³ /day of lube base oils excluding fuels hydrocracker. Total amount (1998 US Gulf Coast): USD 80 million. | | |

Driving force for implementation

To produce distillate with a low wax content.

Example plants

One EU refinery has been identified that uses this process to produce distillates with a low wax content.

Reference literature

[76, Hydrocarbon processing 2011], [183, HP 1998], [191, UBA Austria 1998], [207, TWG 2001].

4.21 Storage and handling of materials

As mentioned before, more information on techniques to consider regarding the storage and handling of materials can be found in the EFS BREF [5, COM 2006]. Among them, the following techniques are those used in the refinery industry.

4.21.1 Underground caverns

Description

More information on all types of caverns can be found in Section 2.21 and in the EFS BREF.

Achieved environmental benefits

- VOC emissions from underground storage caverns are very low or are non-existent. The main reasons are: the temperature of the cavern is low and stable, the product is under pressure and the breathing gases from the cavern are not led to atmosphere but to another cavern.
- The land above caverns is free for other purposes.
- Improves safety.

Cross-media effects

Groundwater leaking into the cavern must be removed and treated with other oily waters.

Applicability

The geology of the site should be adequate to install a cavern, i.e. non-porous rock.

Economics

The construction costs of storage caverns are markedly lower than for above-ground tank farms. In Finland, profitability begins at 50 000 m³ under favourable conditions (highly dependent on the rock type and the hydrocarbon product to be stored). Maintenance costs have been calculated to be one-sixth of those of above-ground tanks.

Driving force for implementation

Prevention of visual intrusion, the reduction of energy consumption, saving of land surface and economic reasons for large storage systems. This technique is one of the safest ways of storing large amounts of hydrocarbon products.

Example plants

Used in some European countries.

Reference literature

[5, COM 2006], [199, Lameranta 2000].

4.21.2 Internal floating roof tanks

Description

As described in the EFS BREF, an internal floating roof tank (IFRT) has both a permanent fixed roof and a floating roof (or deck) inside. The deck in an IFRT rises and falls with the liquid level and either floats directly on the liquid surface (contact deck) or rests on pontoons several centimetres above the liquid surface (non-contact deck). Contact floating roofs can be:

- aluminium sandwich panels that are bolted together, with a honeycomb aluminium core;
- pan steel decks with or without pontoons;
- resin-coated, fibreglass-reinforced polyester (FRP), buoyant panels.

The majority of direct contact floating roofs currently in service are the aluminium sandwich panel type or pan steel type.

More information can be found in Section 2.21 and in the EFS BREF.

Replacement of primary/secondary seals with tighter seals which can reduce VOC emissions might be also applied to IFRTs.

Achieved environmental benefits

Reduction of VOC emissions. Conversion of fixed roof tanks to internal floating roof and seals to minimise evaporation of the product being stored. The control efficiency of this method ranges from 60 % to 99 %, depending on the type of roof and seals installed and the true vapour pressure of the liquid stored. The EFS BREF reports that the emission reductions potential for installing an IFRT with a primary seal ranged from 62.9 % to 97.4 % (estimated using the EPA AP-42 method).

Cross-media effects

The net storage capacity of a fixed roof tank is reduced by approximately 10 %. There is a need to consider flammable atmosphere problems as part of the design.

Operational data

Performance data on emissions and other useful information about IFRT are available in [100, API 2002].

Applicability

IFRTs are widely used in the petroleum industry, however, they are only applicable to vertical fixed roof tanks. An IFRT is less effective in tanks with a small diameter because of the poor effectiveness of the rim seal in small tanks. There are possible compatibility issues between stored products and the IFRT construction materials, e.g. aluminium sheets/pontoons and gasket/sealing materials. Where caustic treatment is included downstream of the process, corrosion on the IFRT might give rise to problems of applicability. Floating suction in existing tanks, high filling rate regimes, mixers and other protuberances all present difficulties in retrofits.

Economics

The costs of retrofits are given in Table 4.72. Costs are dependent on the tank diameter.

Table 4.72: VOC controls in storage

| Emission source | Refinery storage | | |
|--|--|---|--|
| | Internal floating roofs in fixed roof tanks | Secondary/double seals on floating roof tanks | Other roof fitting emission controls (roof legs, still wells) and options (tank paint) |
| Control technology | | | |
| Efficiency | 90 – 95 % | 95 % | Over 95 % when together with secondary seals |
| Investment costs (EUR million) | 0.20 –>0.40 for 20 – 60 metre diameter tanks ⁽¹⁾ | 0.05 – 0.10 for 20 – 50 metre diameter tanks ⁽²⁾ | 0.006 for 50 metre diameter tank ⁽¹⁾ |
| Operating costs | Minor | Replacement every 10 years | Minor |
| Other impacts/comments | Requires tank to be taken out of commission; reduces the net storage by 5 – 10 % | Can reduce maximum storage capacity of tank | Not suitable for high-sulphur crude oils due to pyrophoric scale possibility |
| References: (Installed and retrofitted) | | | |
| ⁽¹⁾ UN-ECE/IFARE, and Industry Propriety Information. | | | |
| ⁽²⁾ UN-ECE/IFARE and Industry Propriety Information (UN-ECE EC AIR/WG6/1998/5). | | | |

Driving force for implementation

European Directive 94/63/EC (Stage 1) prescribes that either fixed roof gasoline storage tanks are fitted with internal floating roofs (with a primary seal in existing tanks and with secondary seals in new tanks) or are connected to a vapour recovery unit. Vapour destruction is also a technically viable option which may be applied, e.g. when vapour recovery is unsafe or technically impossible because of the volume of return vapour.

Reference literature

[5, COM 2006], [100, API 2002], [151, Sema, Sofres 1991], [171, UN/ECE 1998], [207, TWG 2001].

4.21.3 Fixed roof tanks

Description

The fixed roof tank (FRT) can give rise to emissions in the ways described below.

- Filling losses; during tank filling the existing tank vapour space, which is more or less saturated with vapour, is expelled to the atmosphere, while when a tank is emptied the incoming air is slowly saturated with vapours, which are then expelled by subsequent filling and/or breathing. Generally these emissions are greater than standing emissions. A technique to reduce VOC from these tanks is to increase the storage pressure by blanketing.
- Breathing losses; during storage of the liquid there will be vapour emissions from tank breathing caused by the difference in night and day temperatures and by changes in atmospheric pressure. To a certain extent, installing pressure/vacuum relief valves and reducing thermal effects by painting the tank a light colour or fitting insulation can reduce breathing losses.
- Vapours released during water draining.

The technique that is considered to reduce emissions from fixed roof tanks is to install an internal floating roof.

It is to be noted that blanketing tanks by introducing inert gas is a safety measure to avoid an explosive atmosphere but it does not prevent the product from evaporating.

Achieved environmental benefits

The installation of an internal floating roof in fixed roof tanks can reduce VOC emissions up to 90 – 95 % (see Table 4.72).

Cross-media effects

The installation of an internal floating roof in a fixed roof tank requires the tank to be taken out of commission and reduces the net storage by 5 – 10 %.

Operational data

Performance data on emissions and other useful information about FRT are available in [100, API 2002].

Applicability

Fixed roof tanks are typically used for low- or non-volatile material with true vapour pressures (TVP) at less than 14 kPa, e.g. kerosene, heating oil. These tanks can be retrofitted to internal floating roof tanks, but are not suitable for all products, e.g. a bitumen tank with an internal floating roof will not work due to bitumen solidifying in the gap between the wall and the internal floating roof.

Economics

The investment for installing internal floating roofs in fixed roof tanks can be EUR 0.2 – 0.4 million for tanks of 20 – 60 metres in diameter.

Driving force for implementation

Reduction of VOC emissions.

Reference literature

[100, API 2002], [160, Janson 1999], [166, CONCAWE 1999], [207, TWG 2001].

4.21.4 External floating roof tanks**Description**

External floating roof tanks (EFRT) are used to store crudes, light products and intermediate stocks having a vapour pressure of more than 14 kPa but less than 86 kPa at normal storage temperature. More information can be found in Section 2.21 and in the EFS BREF.

With external floating roof tanks (EFRT), filling and breathing losses are greatly diminished in comparison with fixed roof tanks. However, the vapour losses described below are inherent to this type of tank and should be minimised:

- Rim seal and roof-fitting emissions, which result from stock vapour pressure changes due to temperature, and pressure variations, but more importantly wind effects as well as openings in the roof. Standing emissions on external floating roof tanks are generally much more significant than withdrawal emissions.
- Wetting losses by evaporation of liquid from the wet wall, when the level of the liquid is lowered by discharge.
- Vapours released during water draining.
- In many cases, for an external floating roof tank, the emissions through fittings can exceed the rim seal losses especially on tanks with secondary seals. In terms of fitting losses, the major source is from the slotted stilling well (sample well or dipping well).

Techniques to minimise emissions of external floating roof tanks include, but are not limited to, the following:

- installing improved primary seals at the floating deck, e.g. from a vapour-mounted to a liquid-mounted seal;
- installing sleeves around the pipe, incorporating still well wipers;
- installing floats with wipers inside the slotted pipe;
- landing the floating roof tanks as infrequently as possible to avoid unnecessary vapour releases;
- sealing of all floating roof openings (e.g. gauging poles, support legs) with appropriate wrappings, sleeves or compensators;
- installing secondary or tertiary seals between tank walls and roof (see Section 4.21.6);
- designing drains on floating roof tanks appropriately to avoid hydrocarbon contamination of rainwater.

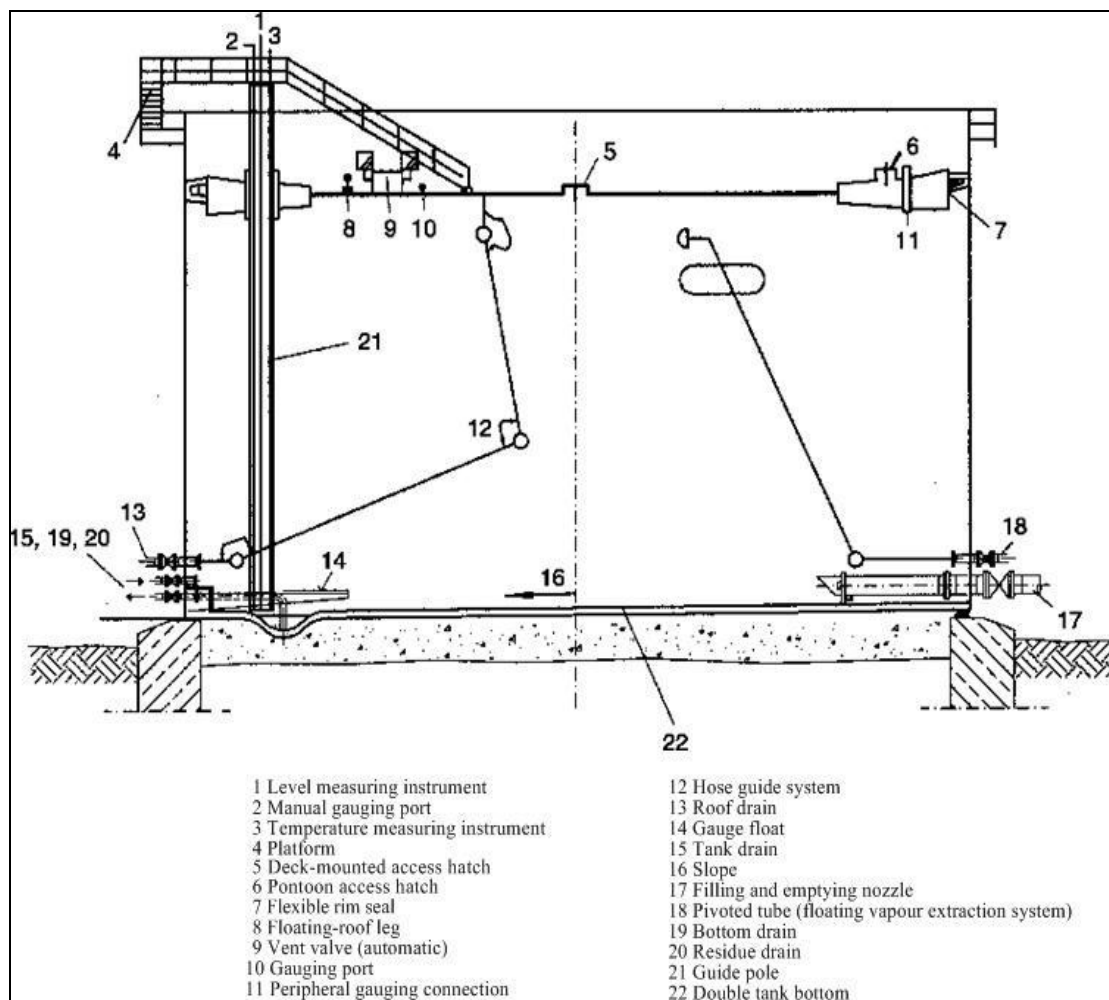


Figure 4.48: Example of a floating roof tank

Achieved environmental benefits

For the same substance, e.g. gasoline, EFRTs have the advantage over fixed roof tanks of significantly lower emissions to the atmosphere of, for example, VOCs. An EFRT can avoid 95 % of the losses from a fixed roof. Product savings give operating benefits.

Cross-media effects

They have potentially more emissions to water than fixed roof tanks, since it is possible for rainwater to enter the tank past the roof seal. Any such water needs to be drained before dispatch of the product to a customer since the quality of the product can be seriously jeopardised.

Operational data

Performance data on emissions and other useful information about EFRTs are available in [100, API 2002]. Examples of emissions reduction efficiency (compared to fixed roof tanks) when retrofitting external floating roofs are given in the following tables [77, REF TWG 2010].

Table 4.73: Tank construction working hypothesis

| Product | Diameter (m) | Height (m) | Calculated annual emissions (kg/yr) ^(*) |
|--|--------------|------------|--|
| Naphtha, heavy | 23 | 14.5 | 3 942 |
| Naphtha, light | 30 | 17 | 2 492 |
| Crude oil | 57 | 16.5 | 5 519 |
| (*) Based on rim seal area, dipping wells/still wells, roof fitting penetrations, without wetting losses. Source: TWG 2010 DE | | | |

Table 4.74: Option of sealing and corresponding expected efficiency

| | Seal construction | Efficiency (%) | | |
|---------------------|---|----------------|----------------|-----------|
| | | Naphtha, heavy | Naphtha, light | Crude oil |
| Case 1 | Double rim seal (fitted secondary seals) dipping wells/still wells not sealed roof legs not sealed | 51.8 | 50 | 95.7 |
| Case 2 | Double rim seal (fitted secondary seals) dipping wells/still wells sealed roof legs sealed | 92.5 | 92 | 98.3 |
| Case 3 | Double rim seal (fitted secondary seals) dipping wells/still wells sealed including helicoat roof legs sealed | 93.3 | 93 | 98.8 |
| Case 4 | Double rim seal (secondary seal with access to pontoon) dipping wells/still wells sealed roof legs sealed | 95.6 | 96.1 | 98.9 |
| Case 5 | Triple rim seal dipping wells/still wells sealed roof legs sealed | 97.1 | 97.5 | 99.1 |
| Case 6 | Triple rim seal dipping wells/still wells sealed + helicoat roof legs sealed | 97.9 | 98.1 | 99.6 |
| Source: TWG 2010 DE | | | | |

Applicability

In retrofit situations where a change in the service of the tank is desired, an acceptable alternative to an EFRT is to retrofit a fixed roof tank with an internal floating cover.

Economics

Investment costs for the retrofitting of a fixed roof tank to an EFRT is EUR 0.26 million per tank of 20 m in diameter. An operator is necessary for tank draining, giving rise to some operating costs.

Driving force for implementation

Directive 94/63/EC (Annex 1) defines an appropriate floating roof tank as one having at least a VOC release efficiency of 95 % as compared with a fixed roof one with no vapour containment controls (that is a fixed roof tank with only a vacuum/pressure relief valve).

Reference literature

[5, COM 2006], [77, REF TWG 2010], [100, API 2002], [142, TWG DE 2012], [151, Sema, Sofres 1991], [196, CONCAWE 2000], [201, Manduzio 2000], [207, TWG 2001].

4.21.5 Pressurised vessels

Pressurised vessels such as bullets and spheres are often fitted with pressure relief valves, which vent to atmosphere or flare. VOC emissions can occur if these valves or bypass block valves have internal leaks. See the EFS BREF.

4.21.6 External floating roof seal systems**Description**

Two or three seals at the external floating roof rim provide a multiple barrier to control VOC emissions from storage tanks. Fitting secondary and tertiary roof rim seals are efficient techniques for emission reduction. When retrofitting rim seals to floating roof tanks for non-waxy products, the second or third seal can be equipped with a contact element for draining the inner tank wall (additional weather seal function). Rim-mounted seals (as opposed to shoe-mounted seals) are favoured, since the former offer emission control if the primary seal fails.

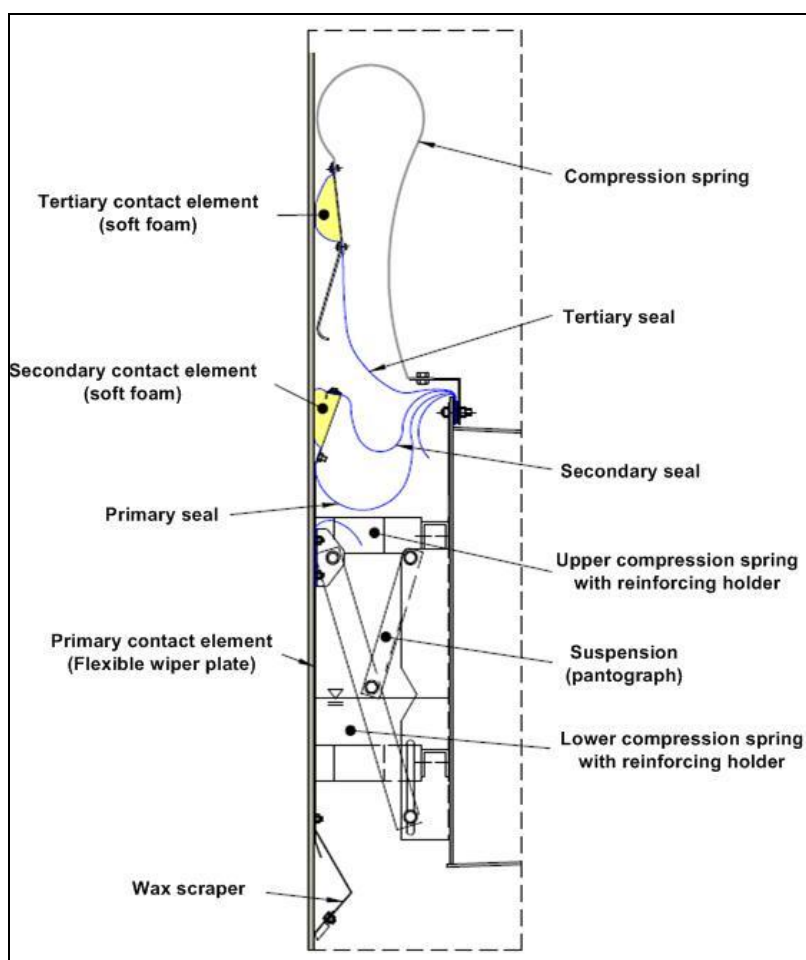


Figure 4.49: Example of multiple seals for external floating roof tank used in a German refinery

Achieved environmental benefits

VOC emissions can be significantly reduced by installing secondary and tertiary seals on storage tanks. The Amoco/US EPA joint study estimated that VOC losses from storage tanks could be reduced by 75 % to 95 % compared to emissions generated by a fixed roof tank of the same capacity without any floating roof. Tertiary seals can achieve a reduction of up to 99 % (see Section 4.21.2). When they are applied to EFRT, secondary seals also reduce the likelihood of rainwater ingress into the tank. Secondary seals for gasoline storage can reduce VOC emissions by up to 95 %.

Cross-media effects

Retrofitting seals usually results in a loss of operating capacity by about 5 %.

Operational data

Performance data on emissions and other useful information about rim seals are available in [100, API 2002].

Applicability

Multiple seals can be readily installed in new units (named double or triple seals) and can also be generally retrofitted (as secondary seals). It is reported to be generally difficult to retrofit tertiary seals.

Economics

Equipping an average tank with a secondary seal system was estimated to cost about USD 20 000 (1991). Investment costs: EUR 0.05 – 0.10 million for tanks with a 20 – 50 metre diameter. Operating costs: replacement likely every 10 years.

Driving force for implementation

European Directive 94/63/EC (Stage 1) prescribes secondary seals for external floating roof tanks and for new internal floating roof tanks for gasoline storage in refineries and terminals.

Example plants

Secondary seals are of common use worldwide. In Sweden, all tanks with light products (Reid vapour pressure higher than 27 kPa) are equipped with double-seal roofs. Tertiary seals are used in several refineries and depots in Germany.

Reference literature

[28, Tebert et al.2009], [100, API 2002], [151, Sema, Sofres 1991], [196, CONCAWE 2000], [207, TWG 2001].

4.21.7 Storage strategy**Description**

The need for certain tanks can often be eliminated through improved production planning and more continuous operations. This technique is closely related to Section 4.15.2. An example is the implementation of an in-line blending system (see Section 4.21.14).

Achieved environmental benefits

Since storage tanks are one of the largest sources of VOC emissions, a reduction in their number contributes to a reduction of VOC emissions. By minimising the number of storage tanks, tank bottom solids and decanted waste water may also be reduced.

Applicability

The reduction in the number of tanks typically requires a full change in the management of product and intermediates. As a consequence, this technique is more easily applied to new units.

Driving force for implementation

Space usage can be improved by reducing the number of storage tanks in operation.

Reference literature

[207, TWG 2001].

4.21.8 Prevention of leakage through tank bottoms

This follows techniques to consider in the determination of BAT for the prevention of leakage through tank bottoms. This topic is well documented in EEMUA publication 183 'Guide for the Prevention of Bottom Leakage from Vertical, Cylindrical, Steel Storage Tanks'.

4.21.8.1 Double bottom tank

Description

Double bottoms can either be retrofitted to existing tanks or incorporated into the design of new tanks. If retrofitted, the existing tank bottom is normally used as the secondary flooring, and sand, gravel or concrete can be installed between the new primary and the secondary floors. In this case, it is general practice to keep the interstitial space to a minimum and therefore the secondary bottom should slope in the same way as the primary bottom. The slopes to the base of tanks can be either straight, cone-up (sloping from the centre down to the tank perimeter) or cone-down (sloping downward from the tank perimeter). Nearly all tank floors are made of carbon steel. If a double bottom is to be installed (either retrofitted or newly built), there are choices in material selection for the new floor. A second carbon steel floor can be utilised or a more corrosion-resistant stainless steel floor can be installed. A third choice is to use a glass fibre-reinforced epoxy coating over the steel.

The use of double bottom tanks allows a vacuum system to be installed, and in this case the space between the lower and upper floors is not filled, but retained as an air space using steel spacers (which can typically be made of steel reinforcement mesh). In this more recent system, the space between the floors is kept under a vacuum that is continuously monitored. Any leak in the primary or secondary floor will dissipate the vacuum and trigger an alarm. A further test of the extracted air will indicate an upper floor failure if product or vapours are present, or a lower floor failure if neither product nor vapours are present (subject to any previous underfloor contamination).

Achieved environmental benefits

Installing a second impervious bottom to a tank provides a measure of protection against non-catastrophic releases due to corrosion, faulty weld joints, or flaws in the bottom material or the construction details. In addition to containment, the secondary bottom provides a means of allowing detection of a bottom leak which is not obviously visible to an operator, as a similar shell defect would be.

Cross-media effects

In the case of retrofitting, the application of this technique may prolong the outage time of tanks during the installation of the double tank bottom. Its application can reduce the capacity of the tank.

Operational data

By installing double tank bottoms, the time between inside inspections and the number of annual tank cleaning procedures are decreased.

Applicability

Applicable to either retrofitted or newly built tanks.

Economics

Typical retrofitting costs for double tank bottoms, as quoted from German and Swiss suppliers, are as follows and include the provision of a vacuum leak detection system:

- carbon steel: EUR 110/m²,
- stainless steel: EUR 190/m²,
- glass fibre-reinforced epoxy: EUR 175/m².

A UK refinery reported that the actual cost of installing a double bottom on a 10 340 m³ tank was EUR 600 000.

Driving force for implementation

Prevention of leaks from storage tanks.

Reference literature

[163, FWE 1999], [197, MWV 2000].

4.21.8.2 Impervious membrane liners**Description**

The impervious membrane liner is a continuous leak barrier under the entire bottom surface of the tanks. It can be an alternative to a double tank bottom or it can be added as an extra measure of safety below the double tank bottom. Like the double tank bottom, it is primarily intended to arrest the small but persistent leaks rather than address a catastrophic failure of the entire tank. The key to an effective liner is that the seams need to be liquid-tight against either the steel shell of the tank or the concrete wall that supports and surrounds the tank. The minimum thickness of the flexible membrane is 1 mm, although 1.5 – 2 mm thick sheets are commonly used. The membrane needs to be chemically resistant to the product stored in the tank.

Achieved environmental benefits

Prevention of leaks from storage tanks.

Cross-media effects

Prolonged tank outage if the liner has to be retrofitted to an existing tank.

Applicability

Impervious membrane liners can be installed either in a new-build design or as a retrofitted design, especially during the overhaul of a tank, and they generally include a leak detection system.

Economics

Recently updated cost data (2011) from UK operators (*source*: UKPIA) are shown in Table 4.75.

Table 4.75: Estimated costs for retrofitting impervious membrane liners to different tanks

| Small tanks | | Medium tanks | | Large tank | |
|---|--------------------------|---|--------------------------|--|--------------------------|
| 3 small tanks (22 m diameter), 20 m (h), sharing a bund | | 3 medium tanks (48.5 m diameter), 20 m (h), sharing a bund | | 1 large tank (81 m diameter), 20 m (h), dedicated bund | |
| Tank volume m ³ (single tank) | 7 603 | Tank volume m ³ (single tank) | 36 949 | Tank volume m ³ | 103 060 |
| Tank footprint m ² (single tank) | 380 | Tank footprint m ² (single tank) | 1 847 | Tank footprint m ² | 5 153 |
| Required bund area (all tanks, 2m wall height)([∘]) | 4 942 | Required bund area (all tanks, 2m wall height) ([∘]) | 24 017 | Required bund area (2m wall height) ([∘]) | 56 683 |
| Cost for installing membrane under the tank floor | | | | | |
| | EUR([∘]) | | EUR([∘]) | | EUR([∘]) |
| Lining of bund floor | 317 755 | Lining of bund floor | 1 672 754 | Lining of bund floor | 4 787 890 |
| Lining bund walls | 282 575 | Lining bund walls | 621 892 | Lining bund walls | 1 038 379 |
| Lining under tanks | 110 079 | Lining under tanks | 535 644 | Lining under tanks | 498 195 |
| Jacking | 680 904 | Jacking | 1 021 356 | Removing and replacing tank floor | 907 872 |
| Total per bund | 1 391 314 | Total cost per bund for a typical installation | 3 851 647 | Total per bund | 7 232 335 |
| Total per tank | 464 150 | Total cost per tank for a typical installation | 1 284 639 | Total cost per tank for a typical installation | 7 232 335 |
| Cost for replacing tank floor, installing new tank foundation | | | | | |
| Lining of bund floor | 317 755 | Lining of bund floor | 1 672 754 | Lining of bund floor | 4 787 890 |
| Lining bund walls | 282 575 | Lining bund walls | 621 892 | Lining bund walls | 1 038 379 |
| Installing new foundation and replacing tank floor | 1 429 898 | Installing new foundation and replacing tank floor | 2 859 797 | Installing new foundation and replacing tank floor | 1 815 744 |
| Total per bund | 2 030 229 | Total cost per bund for a typical installation | 5 154 443 | Total per bund | 7 642 013 |
| Total cost per tank for a typical installation | | | | | |
| Small tank | 676 743 | Medium tank | 1 718 148 | Large tank | 7 642 013 |
| [∘] EUR costs based on currency conversion from GBP of 1.134 84 on 25/07/2011. NB: Required bund area is based on 110 % of the tank rated capacity for the largest tank in the bund. Costs related to project management and design, tank emptying and cleaning are excluded , but expected to be 10 – 15 % of total cost per tank. For large tanks >48.5m in diameter, tank jacking is not an option, therefore costs are based on an estimate for removing and replacing tank floor. Costs related to the need to hire tank space during extended outage to complete works (likely to be 9 months per tank) are also excluded . The lining of bund walls includes fixing at the top of the bund wall, and sealing it to existing bund flooring (where applicable). Installing a new tank foundation after removing the existing tank floor may be a more effective solution where the ground is too permeable or where there is concern that the liner may not remain intact following replacement of the tank. No account has been taken of the increase in business rates following secondary and tertiary containment upgrades. Bund wall lengths are likely to increase depending upon the shape of the bund, also bund height of 2m does not take into account the slope of the bund wall, which will increase the area. Source: CONCAWE/UKPIA 2011 | | | | | |

Driving force for implementation

To prevent soil contamination.

Example plant(s)

Impervious membrane liners are used in lieu of double bottoms in a number of non-European countries.

Reference literature

[151, Sema, Sofres 1991], [207, TWG 2001].

4.21.8.3 Leak detection

Description

As with sewers, one way to protect against soil and groundwater contamination is by detecting leaks at an early stage. Leaks through a tank bottom can be detected by a leak detection system. Conventional systems include inspection ports, inventory control and inspection wells. More advanced systems include electronic sensing probes or energy pulse cables whereby product that comes into contact with the probe or cable will alter its impedance and trip an alarm. In addition, it is common practice to use a variety of inspection procedures on tanks at intervals to prove their integrity. See also Section 4.23.6.1, LDAR programme. Some techniques to consider are:

- equipping storage tanks with overflow alarms and, if appropriate, automatic pump shut-offs;
- installing double bottoms with integrated leak detection systems on tanks where practicable.

It is to be noted that, based on past incidents, a systematic risk analysis is needed to apply the appropriate recommendations to avoid overfilling tanks.

Relief valves on pressurised storage should undergo periodic checks for internal leaks. This can be carried out using portable acoustic monitors or, if venting to atmosphere with an accessible open end, tested with a hydrocarbon analyser as part of a LDAR programme.

Achieved environmental benefits

Prevention of soil and groundwater contamination.

Applicability

Probes and cables have to be packed pretty densely if the leak to be detected is small. Consequently, inspection, where possible, may in some cases be more reliable than probes.

Economics

One refinery reported that the installation of a leak detection system on a group of four 12-metre diameter tanks cost a total of EUR 55 000 with an operating cost of EUR 4 000 per year. The routine inspection of tanks at another refinery was quoted as EUR 2 000/tank per year.

Driving force for implementation

To prevent soil and groundwater contamination.

Reference literature

[197, MWV 2000].

4.21.8.4 Cathodic protection

Description

To prevent corrosion on the underside of the tank bottom, tanks can be equipped with cathodic corrosion protection.

Achieved environmental benefits

Avoidance of soil and groundwater contamination and air emissions due to the prevention of corrosion.

Cross-media effects

Electricity is needed when impressed current cathodic protection (ICCP) requires a DC power source.

Driving force for implementation

To prevent the corrosion of tanks and pipes, and to reduce the maintenance costs.

Reference literature

[101, INERIS 2008], [197, MWV 2000].

4.21.9 Tank farm bund containment

Description

Whereas double tank bottoms or impervious liners protect against the small but incessant leaks, a tank farm bund is designed to contain large spills (for safety as well as for environmental reasons), such as caused by a shell rupture or a large spill from overfilling. The bund consists of a wall or dyke around the outside of the tank to contain all or part of the tank contents in the event of a spill, and (in some cases) an impermeable ground barrier between the tank and the dyke to prevent infiltration of the product into the ground. The dyke is typically constructed of well-compacted earth or reinforced concrete. The height is normally sized to accommodate the maximum contents of the largest tank within the volume enclosed by the dyke. If, due to the local soil conditions, there is a risk of material loss to the substrate then an asphalt, concrete or high-density polyethylene liner may be used to provide a barrier.

Achieved environmental benefits

Containment of large spills from liquid storage tanks.

Cross-media effects

This technique might call for the soil to be compacted, which may be seen as a negative impact. A study in the United States has concluded that the effectiveness of liners in protecting the environment is limited because of their unreliability and the difficulty in inspecting or testing their integrity. Also, there are few releases that would be contained by such liners, and moreover, they are expensive to install. Because of this, it was concluded that other preventative measures are more effective in protecting the environment and are more cost-effective in the long run.

Applicability

In some cases, retrofitting may not be possible.

Economics

Some refineries have quoted the total cost for installing concrete paving under six large tanks at EUR 1.3 million (0.22 million per tank), the cost of sealing the bund dyke walls with asphalt (around 10 tanks) at EUR 0.8 million, and the cost of concrete paving bunds at EUR 70 – 140/m². One refinery quoted the cost of installing 200 m of impermeable HDPE barrier along the site boundary at 150 000 EUR (EUR 750/m).

Driving force for implementation

Containment of large spills that may occur from liquid storage tanks is normally regulated by national laws. In Italy, current legislation foresees for some liquids a volume of the bund less than 100 % of the tank volume. French regulation requires any liquid storage to be associated with a containment volume superior to the highest value from:

- 100 % of the biggest tank volume;
- 50 % of the total capacity of associated tanks.

Reference literature

[174, HMIP UK 1995].

4.21.10 Reduction of the generation of tank bottoms

Description

Minimisation of tank bottoms can be carried out through careful separation of the oil and water remaining in the tank bottom. Filters and centrifuges can also be used to recover the oil for recycling. Other techniques to consider are the installation of side entry or jet mixers on tanks or the use of chemicals. This means that basic sediment and water are passed on to the receiving refineries.

Achieved environmental benefits

Tank bottoms from crude oil storage tanks constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem due to the presence of heavy metals. Tank bottoms are comprised of heavy hydrocarbons, solids, water, rust and scale.

Cross-media effects

Passing the sediments and water from the crude oil tanks to the refinery means that they will most probably show up in the desalter.

Reference literature

[174, HMIP UK 1995].

4.21.11 Tank cleaning procedures

Description

For routine internal tank inspections and for the purpose of repair, crude oil and product tanks have to be emptied, cleaned and rendered gas-free. A technique to clean tank bottoms includes dissolving the majority of the tank bottom content (>90 %) with hot diesel fraction at temperatures of around 50 °C, in which it dissolves most of the tank bottom contents and they can be blended after filtration to the crude tanks. Oil tank cleaning is traditionally performed by workers entering the tank and removing sludge manually, thus they are exposed to potentially explosive and toxic atmospheres. Fully automated techniques of tank cleaning are also available typically using the following procedures.

- Installation of the process equipment: low-pressure/high impact nozzles are installed either in the tank roof or through the existing wall manholes and operated over the liquid surface.
- Tank blanketing: an inert gas is injected and monitored to maintain an oxygen level below 8 %, securing non-igniting conditions.
- Desludging and cleaning: the sludge is sucked out and recirculated via the cleaning nozzles, using the oil in the tank as a cleaning agent. If needed, crude oil or gas oil is added and/or the recirculated media is heated to lower the viscosity.
- Oil separation and recovery: part of the sludge is mechanically separated (decanter) without the addition of chemicals.
- Water wash: a final wash with hot water is performed and finally the inert gas is vented.

Achieved environmental benefits

Emissions during the cleaning of tanks arise during natural or mechanical ventilation. With specific measures, e.g. installation of mobile flares, which are currently under development for cleaning crude oil and product tanks, further emission reductions of VOCs of up to 90 % can be expected. Automated tank cleaning techniques working in closed-loop systems, where the atmosphere from the oil tank is degassed, reduce the venting of VOCs to the ambient air.

Cross-media effects

When natural or forced ventilation is used, VOC emissions may be significantly higher during tank cleaning when compared to VOC emissions from normal operation of an oil tank. Due to the recirculation of water, automated cleaning achieves savings of fresh water and reuse of the

oil as a cleaning agent. Electricity consumption for the cleaning process and generation of inert gas is higher than for manual cleaning. Solid and liquid waste is reduced by using automated cleaning. Closed-loop systems under inert conditions lead to safer conditions, as risk of explosion and human exposure to hazardous substances are reduced.

If the refinery operates its own sludge incineration plant, cleaning residues can be supplied to it.

Operational data

The emissions arising during the cleaning of crude oil tanks and the reduction of these emissions are exhaustively described in [222, UBA 2000]. The use of hot diesel to clean up the tank bottoms requires heating. The corresponding consumption is strongly dependent on the type and size of tank and the type of residues processing. According to information from a supplier of automated tank cleaning [102, ORECO 2011], the following operational data are reported.

Table 4.76: Typical crude oil tank cleaning utility requirements

| | Automated cleaning | Manual cleaning |
|---|---|--|
| Hydrocarbon emissions | 1 – 2 tonnes | 30 – 50 tonnes |
| Fuel consumption | 30 000 – 70 000 litres depending on the need for heating | 20 000 – 25 000 litres |
| Waste for incineration | 20 – 50 m ³ | 2 000 – 5 000 m ³ depending on the volume used for cleaning |
| Waste water | 20 – 50 m ³ | Approx. 500 m ³ |
| NB: Crude oil tank: diameter 50 – 80 m - floating roof - 2 000 m ³ oil sludge. | | |

Applicability

Tank cleaning procedures are generally applicable. Applicability may nevertheless be limited by the type and size of tanks and the type of residue processing.

Economics

The operational costs given in Table 4.77 are typical for crude oil tank cleaning [102, ORECO 2011].

Table 4.77: Typical crude oil tank cleaning estimated costs

| | Automated cleaning | Manual cleaning |
|---|---------------------------|------------------------|
| Direct cleaning cost | 300 000 | 200 000 |
| Waste transportation | 5 000 | 100 000 |
| Waste disposal or processing | 10 000 | 200 000 |
| Overall costs (EUR) | 315 000 | 500 000 |
| NB: Crude oil tank: diameter 50 – 80 m - floating roof - 2 000 m ³ oil sludge. | | |

Driving force for implementation

To reduce VOC emissions and tank bottom content.

Example plants

Examples exist of applications in many EU refineries and tank farms.

Reference literature

[102, ORECO 2011], [167, VDI 2000], [170, REPSOL 2001], [222, UBA 2000], [228, TWG 2000].

4.21.12 Colour of tanks**Description**

It is preferable to paint tanks containing volatile materials a light colour for the reasons given below.

- To prevent increasing the evaporation because of increased product temperature.
- To prevent increasing the breathing rate of fixed roof tanks. A total heat reflectance coefficient of a minimum of 70 % is recommended. This coefficient can be achieved by using colours with a low-coating factor, e.g. white (1.0) or aluminium silver (1.1). In contrast, any of the other colours usually used, including light grey, show significantly higher factors (>1.3), which do not allow the coefficient mentioned above to be achieved.

Achieved environmental benefits

Reduction of VOC emissions.

Cross-media effects

Depending on the geographical landscape context, painting in light colours can result in tanks being more 'visible' but can have a negative visual effect. Emissions may occur while painting is taking place.

Applicability

Painting the roof and the upper part of the shell of a tank in the middle of a tank farm can be almost as effective as painting the entire tank.

Driving force for implementation

Using this technique is also a requirement of Directive 94/63/EC for gasoline tanks, except where there are derogations for visually sensitive areas.

Reference literature

[28, Tebert et al. 2009], [205, Jansson 2000], [207, TWG 2001], [222, UBA 2000].

4.21.13 Other good storage practices**Description**

Proper material handling and storage minimise the possibility of spills, leaks and other losses which result in waste, air emissions and emissions to water. Some good storage practices are listed below (other useful information is available in the EFS BREF [5, COM 2006]).

- Use larger containers instead of drums. Larger containers are reusable when equipped for top and bottom discharge, whereas drums have to be recycled or disposed of as waste. Bulk storage can minimise the chances of leaks and spills as compared to drums. In terms of applicability: safe disposal of non-refillable large containers can be a problem.
- Reduction of the generation of empty oil drums. Bulk purchasing (via tank trucks) of frequently used oils and filling tote bins as intermediate storage. Personnel could then transfer the oils from the tote bin to reusable drums, buckets, or other containers. This would reduce the generation of empty drums and their associated handling costs.
- Storage of drums off the floor to prevent corrosion through spills or concrete 'sweating'.
- Keeping containers closed except when removing material.

- Practise corrosion monitoring, prevention and control in underground piping and tank bottoms (related to Section 4.21.8).
- Tanks for storage of ballast water may cause large VOC emissions. They can therefore be equipped with a floating roof. These tanks are also relevant as equalising tanks for the waste water treatment system.
- Passing of vents from sulphur storage tanks to sour gas or other arrestment systems.
- Vent collection and ducting from tank farms to central abatement systems.
- Installation of self-sealing hose connections or implementation of line draining procedures.
- Installation of barriers and/or interlocking systems to prevent damage to equipment from the accidental movement or driving away of vehicles (road or rail tank cars) during loading operations.
- Implementation of procedures to ensure that arms are not operated until inserted fully into the container to avoid splashing where top-loading arms are used.
- Application instrumentation or procedures to prevent overfilling of tanks.
- Installation level alarms independent of the normal tank gauging system.

Achieved environmental benefits and Economics

| Techniques | Emission factor for NMVOC (g/t throughput) | Abatement efficiency (%) | Size (diameter in m) | Cost (EUR) |
|---|--|--------------------------|----------------------|------------|
| Fixed roof storage tank (FRT) | 7 – 80 | | | |
| External floating roof tank (EFRT) | 7 – 80 | | | |
| Internal floating roof tank (IFRT) | 2 – 90 | | | |
| External paint finish in a lighter shade | | 1 – 3 FRT | 12 | 3 900 |
| | | | 40 | 25 400 |
| Installation of an internal floating roof in existing fixed roof tank | | 97 – 99 FRT | 12 | 32 500 |
| | | | 40 | 195 000 |
| Replacement of a vapour-mounted primary seal with a liquid-mounted primary seal | | 30 – 70 EFRT | 12 | 4 600 |
| | | 43 – 45 IFRT | 40 | 15 100 |
| Retrofitting secondary seals on an existing tank | | 90 – 94 EFRT | 12 | 3 400 |
| | | 38 – 41 IFRT | 40 | 11 300 |
| Improvement of primary seal, plus secondary seal and roof fitting control (pontoon and double deck) | | 98 EFRT | 12 | 200 |
| | | 48 – 51 IFRT | 40 | 200 |
| Installation of a fixed roof on an existing external floating roof tank | | 96 EFRT | 12 | 18 000 |
| | | | 40 | 200 000 |
| NB: Columns for abatement efficiency, size and cost are related to the techniques and not to each other. Costs are average costs for the two diameters and abatement efficiencies are ranges for the technique applied to different types of tanks. | | | | |

Reference literature

[5, COM 2006], [148, Irish EPA 1993], [171, UN/ECE 1998], [196, CONCAWE 2000], [205, Jansson 2000], [207, TWG 2001].

4.21.14 In-line blending

Description

Figure 4.50 shows a scheme of an in-line blending system for gas oils.

Achieved environmental benefits

The energy savings realised by in-line blending compared to batch blending can be substantial, especially in electric power consumption. Using in-line blending reduces the total number of handling operations with respect to feed and product streams, which means less filling and emptying of tanks and thus reduces total emission to atmosphere. The numerous valves and pumps can be provided with dual mechanical seals and can be regularly maintained in order to minimise fugitive VOC emissions. In-line blending generally creates more flexibility towards product specifications and product quantities, and represents large savings by avoiding intermediate storage.

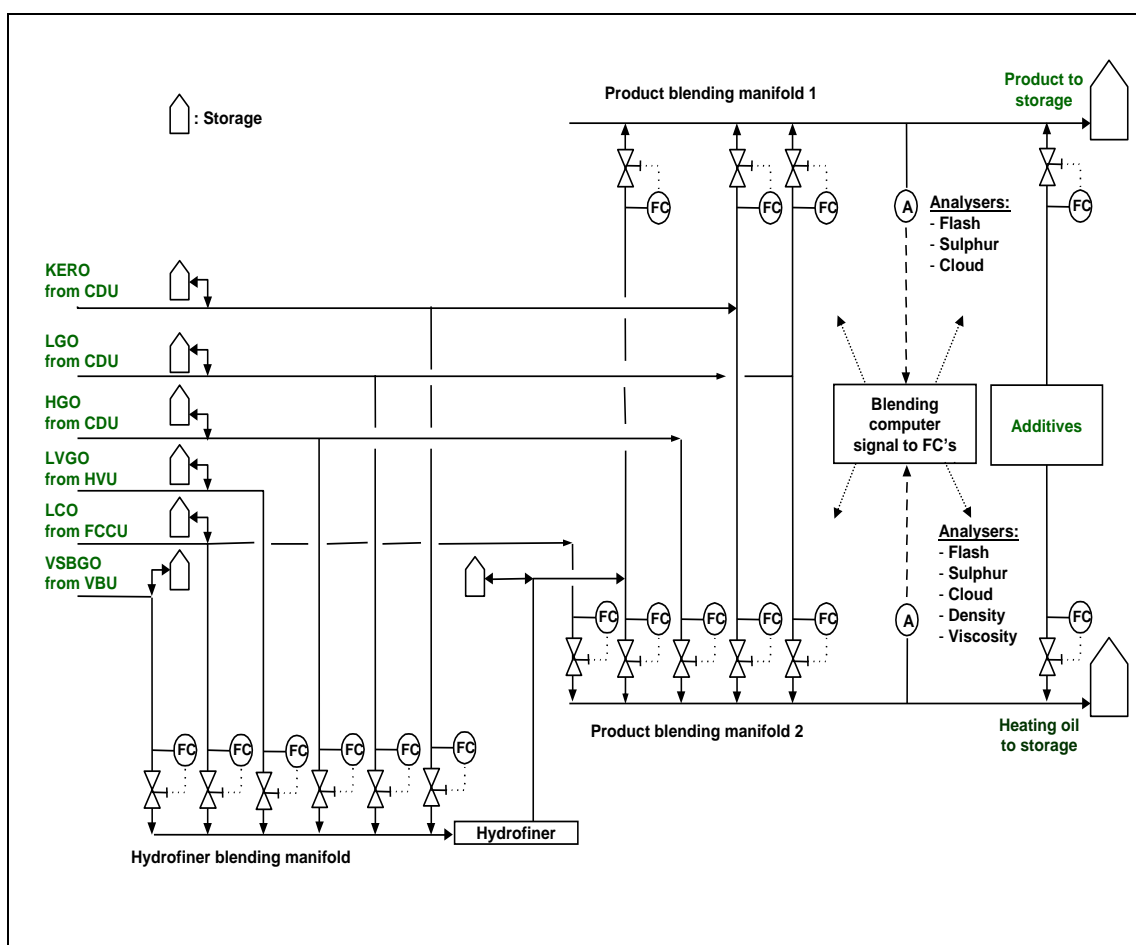


Figure 4.50: Simplified scheme of an in-line blending system for gas oils (automotive diesel and heating oil)

Cross-media effects

In-line blending systems contain many flange connections and valves, which could be sources of leakage, particularly during maintenance.

Operational data

Extreme care has to be taken with in-line quality analysers to ensure the quality of the blended product.

Applicability

Optimising the blend ratios to meet all critical specifications is, to a certain extent, a trial-and-error procedure which is most economically accomplished with the use of a computer. There are usually a number of comparable solutions that give a roughly equivalent total overall cost or profit. Optimisation programs allow the computer to provide the optimum blend to minimise costs and maximise profit.

Example plants

In-line blending systems are normally applied for high volume feed and/or product streams.

Reference literature

[168, VROM 1999].

4.21.15 Batch blending

Description

See Section 2.21.

Applicability

The reasons for batch blending are the minimum storage requirements for strategic reasons, fiscal and tax control, operating flexibility and tank dimensions.

Example plants

For the reasons mentioned above, under Applicability, batch blending of feed and product is still done to a certain extent.

4.21.16 Vapour balancing during loading processes

Description

In order to prevent emissions to atmosphere from loading operations, several options are available. Where loading takes place from fixed roof tanks, a balance line can be used. The expelled mixture is then returned to the liquid supply tank and so replaces the pumped-out volume. Vapours expelled during loading operations may be returned to the loading tank, if it is of the fixed roof type, where it can be stored prior to vapour recovery or destruction. This system can also be used for vessels and barges.

Achieved environmental benefits

Vapour balancing greatly reduces the vapour volumes expelled to atmosphere. It can reduce VOC emissions by up to 80 %.

Cross-media effects

Due to evaporation in the receiving vessel during transfer (vapour evolution by splashing), there is usually a surplus volume of vapours compared to the displaced liquid volume. The balancing line is not considered an efficient means of VOC abatement for the most volatile liquids.

Operational data

Where explosive mixtures can occur, safeguards should be implemented to limit the risk of ignition and ignition propagation. Tanks should remain closed to prevent emissions, so they may operate under a low pressure and ullaging and sampling should not be undertaken through open dispatches. Detonation arrestors require regular cleaning when vapours contain particulates (e.g. soot from badly operated cargo tank inerting systems).

Applicability

Not all vapours can be collected. May affect loading rates and operational flexibility. Tanks which may contain incompatible vapours cannot be linked. Can only be used where the product is pumped out of a fixed roof tank fitted with pressure/vacuum relief valves.

Economics

The investment required is EUR 0.08 million per tank and the operating costs are low.

Driving force for implementation

Reduce VOC emissions.

Example plant(s)

LPG loading. Subsequent loading of transport containers is carried out by means such as closed-loop systems or by venting and release to the refinery fuel gas system.

Reference literature

[166, CONCAWE 1999], [207, TWG 2001].

4.21.17 Bottom loading measures**Description**

The loading/unloading pipe is flange-connected to a nozzle situated at the lowest point of the tank. A vent pipe on the tank can be connected to a gas balancing line, VRU or to a vent. In the last case, VOC emissions can occur. The flange connection in the filling line has a special design ('dry connection') which enables it to be disconnected with minimum spillage/emissions.

Achieved environmental benefits

VOC emissions reduction.

Driving force for implementation

Directive 94/63/EC on the control of VOC emissions for gasoline loading for road tankers.

Reference literature

[156, MCG 1991], [207, TWG 2001].

4.21.18 Tightly sealed floors**Description**

The handling of materials used in the refinery may result in accidental spills that could contaminate the soil, surface water or groundwater. Paving and kerbing the area where materials are handled, for the collection of the possible spilled material.

Achieved environmental benefits

Prevention of soil pollution and directing any spillage of product to the slops. This minimises the volume of waste generated and allows for the collection and reclamation of the material.

Driving force for implementation

To prevent soil and rainwater contamination.

Example plants

Many examples can be found in European refineries.

Reference literature

[156, MCG 1991].

4.22 Visbreaking and other thermal conversions

4.22.1 Visbreaking

4.22.1.1 Hydrovisbreaking

Achieved environmental benefits

A modern technique, which increases the conversion rate of the feed by the addition of H-donators and water without reducing the stability of the process.

Economics

Investment (based on: 750 kt/yr of topped heavy Canadian crude; battery limits including desalting, topping and engineering; 1994 US Gulf Coast). Information is given in Table 4.78.

Table 4.78: Cost comparison between normal and hydrovisbreakers

| Process alternative | Normal visbreaker | Hydro visbreaker |
|---------------------------------------|-------------------|------------------|
| EUR per t/yr | 85 000 | 115 000 |
| Utilities, typical per m ³ | | |
| Fuel oil fired (80 % effic.), kg | 15.1 | 15.1 |
| Electricity, kWh | 1.9 | 12.0 |
| Steam consumed (produced), kg | 15.1 | 30.2 |
| Water, process, m ³ | nil | nil |
| Hydrogen consumption, Nm ³ | NA | 30.2 |

Example plants

Hydrovisbreaking was tested in a 2 Mt/yr visbreaker in a refinery in Curaçao.

Reference literature

[183, HP 1998], [194, Winter 2000].

4.22.1.2 Soaker visbreakers

Description

In this process, a soaker drum is added after the furnace, so the cracking takes place at lower furnace outlet temperatures, and over a longer residence time.

Achieved environmental benefits

The product yields and properties are similar but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption (30 – 35 %) and longer running times before shutting down to remove coke from the furnace tubes (running times of 6 – 18 months versus 3 – 6 months in coil cracking).

Cross-media effects

The advantage of reducing the number of clean-ups for soaker visbreakers is at least partially balanced by the greater difficulty in cleaning the soaking drum.

Operational data

Run times of 3 – 6 months are common for furnace visbreakers and 6 – 18 months for soaker visbreakers. Fuel consumption is around 11 kg FOE/t. Power and steam consumption is similar to the coil one. The operating temperature is 400 – 420 °C at the soaker's exit.

Example plants

Some soaker visbreakers exist in European refineries.

Reference literature

[207, TWG 2001], [221, Italy 2000].

4.22.2 Thermal gas oil unit (TGU)**Description**

For a complete description, see Section 2.22.2 on the thermal gas oil unit.

The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gas oil and naphtha cuts produced.

Achieved environmental benefits

Compared to a conventional visbreaker, the TGU process allows for a significantly higher conversion of the vacuum residue into lighter products. The conversion yield reaches about 40 % w/w instead of 15 % w/w, and the resulting products can be directly valorised in cut streams used for diesel, gasoline and naphtha production.

Cross-media effects

This process increases the site energy consumption and the related air emissions. The net energy necessary for the conversion of the vacuum residue is high. It also generates additional heavily hydrocarbon-contaminated waste waters to be treated in the WWTP.

Operational data

A TGU has been operated at the OMV refinery in Schwechat since Spring 2009. The unit treatment capacity is 2 000 t/day. The heat required for the process is provided by a natural gas-fired gas turbine with a rated thermal input of about 80 MW, which delivers 27 MW_e of additional electrical energy to the refinery grid, together with some process steam generated in the heat recovery unit of this plant.

Applicability

This process is fully applicable for new plants. However, the retrofitting of such a process on existing visbreaking units is not possible.

Economics

The investment amounts to USD 2 400 – 3 000 (EUR 1 900 – 2 500) per bpd (barrel per day) installed, excluding treatment facilities and depending on the capacity and configuration (basis Europe: 2004).

Driving force for implementation

Maximisation of the site conversion ratio towards ‘no residue’ refining.

Example plants

Approximately 12 units are installed worldwide. One plant has been operated since 2009 by OMV in Schwechat (Austria).

Reference literature

[54, Gallauner et al.2009], [76, Hydrocarbon processing 2011], [228, TWG 2000].

4.22.3 Sour gas and waste water management

Description

The gas generated in the visbreaking may be sour and contain sulphur compounds, in which case a gas-sweetening operation, typically amine scrubbing, should be applied before the gas is recovered into products or used as refinery fuel gas. Visbreaking gas, apart from being amine scrubbed to remove H₂S, is further treated to remove approximately 400 – 600 mg/Nm³ of mercaptan sulphur (depending on the feed), in order to meet the refinery fuel gas sulphur content specification.

The aqueous condensate is usually sour, and should be passed to the sour water stripper in an enclosed system.

Achieved environmental benefits

Reduction in the sulphur content of products.

Cross-media effects

Need for chemicals and utilities to run the processes.

Driving force for implementation

Sulphur specifications of the products.

Example plants

Sour gas use and waste water management are applied in many refineries.

Reference literature

[228, TWG 2000].

4.22.4 Reduction of coke formation in visbreakers

Description

During thermal cracking some coke is produced and deposits itself onto the furnace tubes. The coke should be cleaned when necessary. Additives are available on the market to control the sodium content within the feedstock. The control of the addition of caustics or specific additives to the feedstock upstream can also be used.

Achieved environmental benefits

Reduction of the coke formation and, as a consequence, reduction of cleaning waste.

Driving force for implementation

This technique is typically applied to prevent cleaning.

Reference literature

[207, TWG 2001].

4.23 Waste gas minimisation and treatments

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for air emissions from oil and gas refining.

For a given technique, the information provided here aims at completing, broadly, the operational data and material that have already been provided in previous sections where only specific results achieved from the application of this technique to a particular process or unit are reflected. Consequently, general information on environmental benefits, cross-media effects, operational data, and applicability which have not appeared in other sections will be found in this section. Complementing these techniques that may appear within the production activities, this section and the next one also contain end-of-pipe processes which concern the whole refinery and have to be considered as well for the determination of BAT. Under this category are the sulphur recovery units, flares, and amine treatment and the waste water treatments. These techniques are only discussed here.

4.23.1 CO abatement techniques

Description

CO boilers and catalyst reduction of CO (and NO_x). Good primary measures for CO reduction are:

- good operational control;
- constant delivery of liquid fuel in the secondary heating;
- good mixing of the exhaust gases;
- catalytic afterburning;
- catalysts with oxidation promoters.

Achieved environmental benefits

Reduction of CO emissions. Emissions after the CO boiler: <100 mg/Nm³. In the case of conventional firings, a CO concentration below 50 mg/Nm³ is achievable at temperatures above 800 °C, at sufficient air delivery and sufficient retention times (see Table 4.39).

Applicability

FCC and in heavy residues fired. (See Sections 4.10.4.9 and 4.5.5).

Reference literature

[228, TWG 2000].

4.23.2 CO₂ emission control options

For more information, see also Chapter 6 on emerging techniques.

Description

Unlike SO₂, NO_x or particulates flue-gas treatments, a feasible abatement technology for CO₂ is not available. CO₂ separation techniques are available but the problem is the storage and the recycling of the CO₂. Options for the refiner to reduce CO₂ emissions are:

- effective energy management (see Section 4.15.1.2), including:
 - improving heat exchange between refinery streams;
 - integration of refinery processes to avoid intermediate cooling of components (e.g. Section 4.19.1, Progressive distillation unit);

- recovery of waste gases and their use as fuels (e.g. flare gas recovery);
- use of the heat content of flue-gases;
- use of fuels with high hydrogen contents (topic discussed in Section 4.10.2);
- effective energy production techniques (see Section 4.10.3); this means the highest possible recovery of energy from fuel combustion;
- the capture, transport and sequestration (CCS - Carbon Capture and Storage) of CO₂ emissions (see Chapter 6, Emerging Techniques).

As the CCS option is not yet available at site scale, choices for abatement techniques should be made taking into account the possibility to further use the CO₂.

Achieved environmental benefits

Reduction of CO₂ emissions.

Cross-media effects

The use of fuels with high hydrogen contents reduce CO₂ emissions from the refineries but overall will not reduce CO₂ as these fuels will not then be available for other uses.

Operational data

Rational energy use requires good operation to maximise heat recovery and process control (e.g. O₂ excess, heat balances between reflux, product temperature to storage, equipment survey and cleaning). To get optimum results, repeated operator training and clear instructions are necessary.

Reference literature

[77, REF TWG 2010], [196, CONCAWE 2000], [207, TWG 2001].

4.23.3 NO_x abatement techniques

The NO_x emission level of an oil refinery or a natural gas plant is influenced by the refining scheme, the type of fuels used and the abatement techniques implemented. As the number of emission sources and their contribution to the overall emission level may vary greatly, one of the first techniques to consider is the precise quantification and characterisation of the emission sources in each specific case. For more information, see Section 3.26.

See also Section 4.23.8 for information on the SNO_x combined technique.

4.23.3.1 Low-temperature NO_x oxidation

Description

The low-temperature NO_x oxidation process injects ozone into a flue-gas stream at optimal temperatures below 150 °C, to oxidise insoluble NO and NO₂ into highly soluble N₂O₅. The N₂O₅ is removed in a wet scrubber by forming dilute nitric acid waste water, which can be used in plant processes or be neutralised for release.

Achieved environmental benefits

Low-temperature NO_x oxidation can achieve 90 – 95 % removal of NO_x, with consistent NO_x levels as low as 5 ppm. Additional benefits are the heat recovery from the fuel gas, which remains fully possible. The entire process is controlled to produce no secondary gaseous emissions. Because ozone is used as an oxidising agent, emissions of CO, VOCs and ammonia are also reduced.

Cross-media effects

Ozone should be produced on site, on demand, from stored O₂. There is a risk of ozone slip.

Low-temperature oxidation (LoTO_x) should be necessarily associated with a new or existing scrubbing unit, and generates waste water to be treated properly. An increase in nitrate load to the existing WWTP might have to be considered, together with the associated cost to control nitrates. Nitric acid is produced and needs to be neutralised, with an alkali used in the scrubbing section.

Operational data

The use of ozone and the low optimal temperatures of the process provide stable treatment conditions. Energy consumption for the production of ozone range from 7 to 10 MJ/kg (2–2.8 kWh/kg) of ozone produced, with a concentration of 1–3 % w/w with dry oxygen feed. Temperatures should be below 150 °C to minimise ozone decomposition. Heavy particulate-laden fuels may require additional equipment.

Applicability

This process has been developed and is known as SNERT (scrubber-based NO_x emissions reduction technology). The NO_x-removal performance is directly linked to the ozone injection rate and its real-time regulation in relation to the NO_x outlet concentration target. The outlet NO_x can be adjusted by varying the set point on the system controller.

This process can be used as a stand-alone treatment system or can follow other combustion modifications and post-combustion treatment systems, such as low-NO_x burners, SCR or SO_x removal, as a final polishing step, including the treatment of ammonia slips. It can be easily retrofitted to an existing plant.

Economics

This technique requires low maintenance and low operator interface. The relative capital costs and operating costs given by the technology providers claim that they are equal to, or less than, SCR-type systems.

A prospective study for the potential control of existing major SO₂ and NO_x industrial sources in Colorado (US) provides accumulative capital and operational annual cost data expressed per tonne of abated NO_x for some industrial sectors. In refineries, the quoted application (using updated economic data from US EPA for 2005) concerns FCC units with costs ranging from EUR 1 391 – 1 595 per tonne (USD 1 884 – 2 161 per tonne – based on currency conversion rate of 0.73822 on 1/07/2007). As a comparison, other cost ranges are available for wet kilns EUR 2 303 – 2 454 per tonne (USD 3 102 – 3 324 per tonne) and dry kilns EUR 1 717 – 1 963 per tonne (USD 2 327 – 2 659 per tonne) in the cement industry.

Example plants

The process is in use in US commercial installations in sectors such as acid pickling, lead smelting, steam boilers and coal-fired boilers. Also, a number of FCC units have been notably retrofitted with such a technique in the US (see Section 4.5.4.5).

Driving force for implementation

To reduce NO_x emissions.

Reference literature

[17, Jeavons & Francis 2008], [183, HP 1998], [207, TWG 2001], [242, Crowther 2001].

4.23.3.2 Selective non-catalytic reduction (SNCR)

Description

SNCR is a non-catalytic process for removing nitrogen oxides from combustion flue-gases by gas phase reaction of ammonia or urea at high temperatures (generally between 850 °C and 1 100 °C). This technique, also called thermal DeNO_x, reduces NO_x to nitrogen and water. To achieve a good mixing, the small amount of reactant is injected along with a carrier gas, usually

air or steam. General information about this technique can be found in the CWW BREF [6, COM 2003] and in the LCP BREF [7, COM 2006].

Achieved environmental benefits

Reductions of 25 – 70 % can be achieved, giving values of less than 200 mg/Nm³.

Cross-media effects

An intrinsic limitation of the SNCR technique is the emission of a small amount of unreacted NH₃ (ammonia slip) in the flue-gas stream. The ammonia slip is typically in the range of 5 – 20 ppm (3 – 14 mg/Nm³), the higher values being associated with higher NO_x reduction. The US EPA identified ammonia as the single largest precursor of fine particulate (air pollution (2.5 microns and smaller) in the country.

A side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphates give rise to the fouling and corrosion of downstream equipment.

Aqueous ammonia, anhydrous ammonia, or urea can be used as a reactant in the SNCR system. The storage of gaseous or liquefied anhydrous ammonia has a great hazardous potential. Therefore, whenever possible, after an appropriate evaluation of the risks, a liquid solution of ammonia (25 %) or urea should generally be used.

N₂O is a by-product formed when SNCR is used. Urea-based reduction generates more N₂O than ammonia-based systems. At most, 10 % of the eliminated NO_x is formed into N₂O in the urea-based systems [103, EPA 2002].

Operational data

The NO_x reduction rate depends very much on the possibility of matching the following temperature windows together with a minimum residence time of 0.2 – 0.5 s in the temperature window:

- 850 – 1 000 °C, for ammonia and caustic ammonia (optimum 950 °C);
- 800 – 1 100 °C, for urea (optimum 1 000 °C).

Injection of reagent below this temperature window results in excessive ammonia slip. Injection of reagent above the temperature window results in increased NO_x emissions. In some applications, it has been suggested that chemical enhancers, such as hydrogen, are needed to help the reaction at lower temperatures, but this type of application is not reported within the refining industry.

The ammonia produced in the sour water stripping (see Section 4.24.2) can be used as a DeNO_x agent. It also depends on the NO_x inlet concentration to be abated, because even under optimal thermal conditions, there is a lower limit to the technically achievable reduction yield and outlet concentration due to the particular mixing conditions and chemical kinetics.

Applicability

SNCR is typically applied to flue-gases from heaters and boilers. There are only very small space requirements, mainly concerning NH₃ storage.

In some cases, operating and physical constraints can make retrofitting difficult, e.g. the temperature window required may occur in the middle of the boiler tube bank and could lead to impingement of the injected chemical against the tubes.

Economics

Cost considerations include the initial capital costs for modifying the furnace or boiler, piping to inject the reactant, the reactant supply system, and the recurring cost for ammonia or urea to react with the NO_x. For specific cost-effectiveness data, see Sections 4.5.4.2 and 4.10.4.6.

Driving force for implementation

To reduce nitrogen oxide emissions.

Example plants

Applied to FCC units, process furnaces and boilers.

Reference literature

[103, EPA 2002], [104, Tayyeb Javed et al.2006], [166, CONCAWE 1999], [182, Ecker 1999], [183, HP 1998], [191, UBA Austria 1998], [207, TWG 2001], [222, UBA 2000].

4.23.3.3 Selective catalytic reduction (SCR)**Description**

Also known as catalytic DeNO_x. The ammonia/urea vapour is mixed with the flue-gas through an injection grid before being passed through a catalyst to complete the reaction. Various catalyst formulations are available for different temperature ranges: zeolites for 300 – 500 °C, traditional base metals employed between 200 °C and 400 °C, and metals and activated carbon for the lowest temperature applications (150 – 300 °C). More information about this technique can be found in the CWW BREF [6, COM 2003] and the LCP BREF [7, COM 2006].

Achieved environmental benefits

SCR is especially suitable for situations where emission standards are strict. With SCR, removal efficiencies of 80 – 95 % can be achieved generally for inlet concentrations over 200 mg/Nm³. Residual NO_x stack levels of 10 – 20 mg/Nm³ can be achieved by application of SCR in gas-fired boilers and furnaces. When firing heavy residues, emissions of <100 mg/Nm³ (3 % O₂, half-hourly mean value, efficiencies of up to 90 %) can be achieved.

Cross-media effects

The main cross-media effects can be summarised below.

- As with SNCR, an intrinsic limitation of the SCR technique is the emission of a small amount of unreacted NH₃ (ammonia slip) in the flue-gas stream. The ammonia slip is typically in the range of 2 – 10 ppm (1.4 – 7 mg/Nm³ at 25 °C), the higher values being associated with higher NO_x reduction and, more specifically, with catalyst end-of-run conditions. It should be noted that ammonia slip is dependent on many factors, including NH₃ injection rate, catalyst activity, flue-gas distribution, process controllability.
- The spent catalyst should be disposed of properly.
- As for SNCR, aqueous ammonia, anhydrous ammonia, or urea can be used as a reactant in the SCR system. The storage of gaseous or liquefied anhydrous ammonia has a great hazardous potential. Therefore, whenever possible, after an appropriate evaluation of the risks, a liquid solution of ammonia (25 %) or urea is generally preferred.
- A small amount of SO₂ is oxidised to SO₃ over the SCR catalyst. In sufficient amounts, SO₃ in flue-gas may impact plume opacity.
- Additional fuel consumption may be needed to increase the furnace flue-gas temperature to reach the one required by the catalyst. In this case, additional CO₂ emissions will be produced (see under Operational data and Economics).

Operational data

The theoretical amount of reducing agent for removing 1 kg of NO_x is dependent on the ratio of NO to NO₂ in the combined NO_x concentration, as reaction stoichiometry requires one mole of ammonia to reduce one mole of NO and two moles for one mole of NO₂. Attention is required for applications where fouling substances like SO₃ and soot or dust are present in the off-gas. The presence of SO₃ and ammonia can lead to the formation of ammonium sulphates if the flue-

gas temperature drops below the ammonium salt deposition temperature. Ammonium sulphates may have a detrimental effect on the catalyst due to the masking of active sites and can lead to fouling of downstream heat exchangers. Catalyst deactivation can be mitigated by ensuring that the process unit is operated above the ammonium salt deposition temperature.

The catalyst has a general lifetime of 4 to 7 years for oil firing, and 7 to 10 years for gas firing, but shorter lifetimes have been reported in particularly unfavourable conditions. For the multi-fuel SCR catalyst, the catalyst life is likely driven by the most severe fuel. The pressure drop of the catalyst bed will lead to a minor amount of additional power consumption from fans in the system or loss of efficiency in the case of a gas turbine application (equivalent to 0.5 – 1 % of the heat input).

Flue-gas reheat may be required if the SCR is located downstream of wet scrubbing processes or in applications with low flue-gas temperatures. The minimum operating temperature for a SCR unit is dependent on catalyst type and composition and will be application-specific. According to a study at API refinery (Italy), the fuel gas required to increase the temperature (to around 270 °C) could lead to additional CO₂ emissions, in the order of magnitude of 5 750 tonnes/yr for 100 tonnes of NO_x abated.

At Preem Gothenburg Refinery (SE), the SCR used at the reformer unit is of the low-temperature type (185 °C) and achieves 90 % reduction of NO_x. At Preem Lysekil Refinery (SE), the SCR used at the FCC unit reports a NH₃ slip <5 ppm (<3.5 mg/Nm³), based on continuous monitoring from 2010 to 2011.

Applicability

(SCR) has been applied to combustion flue-gases or process off-gases (e.g. FCC). The introduction of a SCR system into an existing installation is a challenge due to space, pressure and temperature problems. Creative solutions can often be found to reduce the retrofit costs. Higher operating temperatures reduce the catalyst size and costs but introduce retrofit complexity. Lower operating temperatures increase the required catalyst volume and costs but often allow for a more simple retrofit.

So far, operating temperatures between 200 °C and 450 °C prevail. These temperatures are normally available before the economiser section or the air preheater of a boiler. Gas-fired refinery furnaces generally have a stack temperature of 150 – 300°C. Dependent on the flue-gas sulphur content, a medium-temperature (MT) or low-temperature (LT) catalyst can be applied in tail-end configuration. Zeolite-type catalysts have reached the marketplace. In the US, a number of gas turbines have been fitted with these catalysts.

Combined techniques for both SO₂ and NO_x removal also use such a catalyst, e.g. the DeSoNO_x process [7, COM 2006]. As for oil firing, only MT catalysts can be applied, because of the presence of sulphur and particulates. MT catalysts have been widely applied in coal-fired power plants predominantly under conditions where the flue-gas still contains all the fly ash and SO₂ from the boiler. Two other configurations are low dust/high SO₂ level and low dust/low SO₂ level (tail-end configuration).

There is little experience of the use of SCR for units applying vacuum residue as fuel. However, the power plant of the TOTAL Mitteldeutschland refinery in Germany uses vacuum residue, visbreaker residue and FCC slurry as fuel in its three oil-fired heaters. A SCR plant in high dust configuration is installed after the heaters, cleaning the gas of the NO_x to concentrations lower than 150 mg/Nm³ (see Section 4.10.4.7 for detailed data-sets). Unabated fly ash concentrations for oil firing are in the range of 100 – 600 mg/Nm³ (with the highest values for vacuum residues). SCR applied under these conditions may suffer from clogging by fly ash and sulphates. The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 – 4 %).

Pressure drop can be important when considering whether SCR can be applied to a flue-gas system. For this reason natural draft furnaces could probably not be fitted with it. See Section 4.23.8 for information on the SNO_x combined technique.

Economics

See applications in each section (Section 4.10.4.7 for the energy system, Section 4.5.4.1 for FCC units and Section 4.5.4.1, and Section 4.7.8.3 for cokers). The investment for a new SCR system depends largely on the flue-gas volume, its sulphur and dust content and the retrofit complexity. For existing installations, the possible location of the catalyst bed is often constrained by space limitations, which will lead to additional retrofitting costs.

The installation of two SCR units was studied in 2007 at the API refinery (Italy) with the objective of reducing NO_x emissions from gas furnaces: one at the thermal cracking unit, for an estimated investment cost (ammonia system, compressor, design and installation) of EUR 2.2 million, and the other one at the pipestill furnaces, for EUR 3 million. Both SCR had designed performances of 85 – 87 % NO_x abatement (from average 120 mg/Nm³, with current low-NO_x burners, to 15 mg/Nm³) and a flue-gas flow of around 55 000 Nm³/h. The project was not completed.

Table 4.79 gives data on the cost-effectiveness of the use of SCR under different conditions.

Table 4.79: Data on the cost-effectiveness of SCR retrofitting for various refining units

| SCR | Cost-effectiveness in EUR/tonne NO _x removed (includes capital charge of 15 %) |
|---|---|
| Heaters and boilers firing refinery blend gas | 8 300 – 9 800 |
| | 12 000 |
| | 4 200 – 9 000 |
| Boilers firing residual fuel oil | 5 000 – 8 000 |
| | 4 500 – 10 200 |
| Gas turbines firing natural or refinery blend gas | 1 700 – 8 000 |
| Fluid catalytic cracking units | 2 800 – 3 300 |

Driving force for implementation

To reduce NO_x emissions.

Example plants

SCR has been applied to FCC off-gases, gas turbines, process boilers and process heaters. It has been applied successfully in a large variety of applications: coal- and oil-fired power plants, waste incineration plants, diesel and gas engines, gas turbine plants, steam boilers and refinery furnaces (such as naphtha reformers, steam reformers, crude and vacuum distillation units, thermal cracking and hydroprocessing units) and FCC plants. There has been less experience with flue-gas from firing high-sulphur residual oil.

SCR is used extensively in power plants in Japan, Germany and Austria and in gas turbine plants in the Netherlands and in California in the US. SCR is also widely used in waste incineration plants. To date, SCR has been successfully applied worldwide in refinery processes as power plants and FCCs. For example, at refineries in Japan, SCR applications are common. In European refineries, more than six applications have been found (Austria, the Netherlands and Sweden).

Reference literature

[77, REF TWG 2010], [105, EPA 2002], [166, CONCAWE 1999], [168, VROM 1999], [176, R. E. Constructors 1998], [182, Ecker 1999], [200, Gilbert 2000], [183, HP 1998], [207, TWG 2001], [222, UBA 2000].

4.23.4 Particulates

Particulate matter (PM) emissions from refinery units entail particles present in the flue-gas from furnaces, particularly soot, catalyst fines emitted from FCC regeneration units and other catalyst-based processes, from the handling of coke and coke fines and ash generated during the incineration of sludges. Particulates generated in the refinery contain metals. Therefore, a reduction in the particles content reduces the metal emissions from the refinery. The particles may range in size from large molecules, measuring a few tenths of a nanometre, to the coarse dusts arising from the attrition of catalyst. Distinction is usually made between aerosols, $<1 - 3 \mu\text{m}$ and larger dust particles. The avoidance of fine particulates $<10 \mu\text{m}$ (PM_{10}) is particularly important for health reasons.

The available dust removal techniques can be subdivided into dry and wet techniques or a combination of the two. The usual techniques applied at refineries for dust emission reduction are briefly discussed below. The main dedusting processes' dry techniques include cyclones, electrostatic precipitators and bag filters. Some wet techniques such as scrubbers may also be used, mainly as a finishing treatment.

4.23.4.1 Cyclones

Description

The principle of cyclone separation is based on centrifugal force, whereby the particle is separated from the carrier gas. More information can be found in the CWW BREF [6, COM 2003]. Data on the application of cyclones to FCC units is available in Section 4.5.5.1.

Achieved environmental benefits

Cyclones are used to reduce dust concentrations in the $100 - 500 \text{ mg/Nm}^3$ range. A novel cyclone design, called the rotating particulate separator (RPS), is able to effectively remove particles of $>1 \mu\text{m}$; this design, however, has a limited capacity compared to the conventional cyclone. Third cyclones achieve a 90 % reduction of particulate emissions ($100 - 400 \text{ mg/Nm}^3$). Modern multi-cyclones used as third-stage cyclones achieve an 80 % reduction of particulate emissions to about 50 mg/m^3 .

Cross-media effects

By nature, cyclones are efficient for larger particulates but do not separate and retain the finest part of emitted dust. Furthermore, a reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem.

Operational data

Cyclones can be designed for high temperature and pressure operation. Dust collection equipment is normally simple to operate and fully automated. For dry separation, no utilities are needed. For dust removal, normally no additives are used. Sometimes the collected dust needs rewetting to prevent the spreading of dust during handling.

Applicability

Multi-cyclones as employed in FCC units or cokers are not able to remove fine particulate matter ($\text{PM}_{10} = \text{dust} <10 \mu\text{m}$) and therefore they are mainly used as a pre-separation step.

Driving force for implementation

Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalytic fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

In refineries, multi-cyclones are employed, often together with ESPs, in FCC and RCC units.

Reference literature

[168, VROM 1999], [194, Winter 2000].

4.23.4.2 Electrostatic precipitator (ESP)**Description**

The basic principle of operation for electrostatic precipitators (ESP) is simple. Flowing gas is ionised as it passes between a high-voltage electrode and an earthed (grounded) electrode. The dust particles become charged in the electric field that is generated and are attracted to the earthed electrode. The precipitated dust is removed from the electrodes mechanically, usually by vibration force (dry ESP), or by water wash (wet ESP).

Achieved environmental benefits

ESPs are capable of collecting bulk quantities of dust including very fine particles at high efficiencies. ESPs can achieve values of $<10 - 50 \text{ mg/Nm}^3$ (95 % reduction or higher with higher inlet concentrations only). However, a penetration 'window' exists in the submicron (0.1 – 1 μm) size range where the collection efficiency lowers.

Cross-media effects

Electricity consumption, dust disposal, and in some cases ammonia emissions. In addition, the high voltage in an ESP introduces a new hazard in refineries. For some installations, ammonia may be injected to improve ESP performance. For these installations, ammonia emissions result from ammonia slip through the ESP. The dust collected in an ESP requires disposal if a useful outlet is not found.

Operational data

An ESP uses some electricity. For dust removal, normally no additives are used. Sometimes the collected dust needs rewetting to prevent the spreading of dust during handling.

Applicability

The application of ESPs can be found in FCC units, FGD processes, power plants and incinerators. It may not be applicable for some particulates with high electric resistance. They typically can be installed in new and existing plants.

Economics

Some recent examples of ESP costs for FCC units are available in Section 4.5.5.2. Generally, fines disposal costs are not included and need to be taken into account for the total cost.

Driving force for implementation

Process gas streams must often be cleaned to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

In refineries, multi-cyclones and ESPs are employed in FCC units and in heavy oil and residue cracker units.

Reference literature

[106, Bong-Jo Sung et al.2006], [168, VROM 1999], [194, Winter 2000].

4.23.4.3 Filtration

Description

Fabric and solid bundle blowback filters (see also Section 4.5.5.3.).

Achieved environmental benefits

Fabric and solid bundle blowback filters can achieve values less than 5 mg/Nm^3 . They are more efficient than cyclones and ESPs on the finest particulates. Solid bundle filters can allow a filtration that is guaranteed for particulates above a minimal granulometry of $0.8 - 1 \text{ }\mu\text{m}$.

Cross-media effects

As for all other dry separation techniques, a reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift from an air emissions problem to a waste problem. In the case of conventional fabric bundles, filter material life is limited (1 – 2 years) and may create a disposal problem. In the case of solid ceramic/alloy bundles, the lifetime is much longer but bundles may need chemical cleaning from time to time if an eventual progressive increase of the pressure drop due to plugging is experienced, generating another issue of waste elimination.

Operational data

Dust collection equipment is normally simple to operate and is fully automated. For dry separation, limited utilities are needed.

Applicability

Fabric filters are effective, except in applications with sticky dust or at temperatures of over $240 \text{ }^\circ\text{C}$. Depending on the flow rate design parameters, they can reach significant volumes and space needs.

Solid bundle filters are much more compact, and can resist much higher temperatures, up to $800 \text{ }^\circ\text{C}$, depending on the metallurgy of the bundle's constituents.

Filters are typically used for the cleaning of flue-gases with an output of $<50\,000 \text{ Nm}^3/\text{h}$, even if they are also used for the treatment of much higher flow rates in the metallurgy. They are well adapted for processes likely to deliver variable flue-gas flows and dust concentrations.

Driving force for implementation

Process gas streams must often be cleaned to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors and turbo expanders. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Reference literature

[168, VROM 1999], [194, Winter 2000].

4.23.4.4 Wet scrubbers

Description

In wet scrubbing, the dust is removed by countercurrent washing with a liquid, usually water, and the solids are removed as slurry. Venturi and orifice scrubbers are simple forms of wet scrubbers. The electrodynamic Venturi (EDV) washer reduces the dust emission to 5 mg/Nm^3 . The technique combines Venturi with electrostatic dust separation. EDV is reported to be used in the flue-gas treatment of combustion installations and incinerators. More information is available in the WI BREF [81, COM 2006].

Achieved environmental benefits

A hypothetical curve (US EPA) illustrating particle size and collection efficiency for wet scrubbers is shown in Figure 4.51. Wet scrubbers reduce between 85 % and 95 % of the

particulates and can achieve values of particulate concentration of $<30 - 60 \text{ mg/Nm}^3$. In addition to solids removal, wet scrubbers can be used to simultaneously cool the gas and neutralise any corrosive constituents. The collecting efficiency can be improved by the use of plates or packings at the expense of a higher pressure drop.

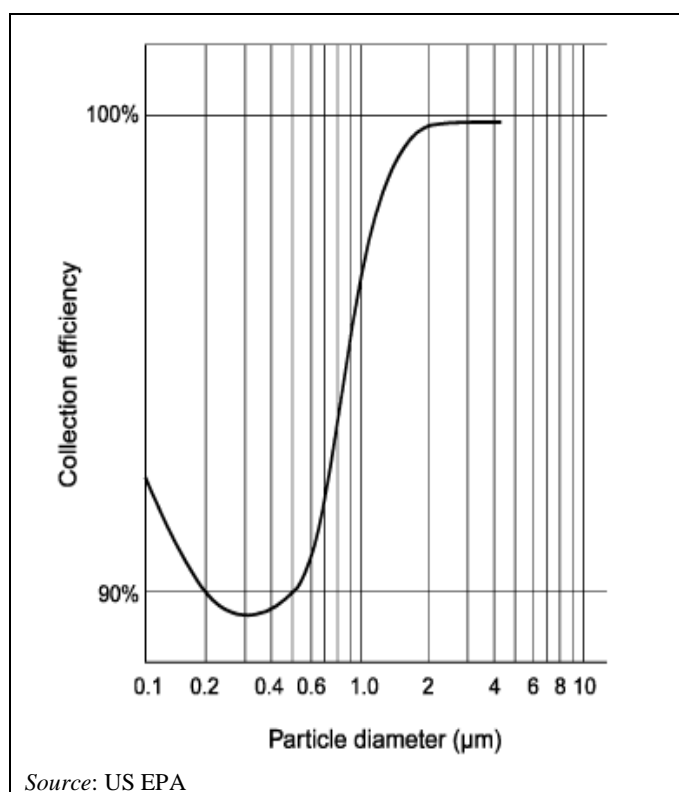


Figure 4.51: Wet scrubber collection efficiency

Cross-media effects

A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift from an air emissions problem to a waste problem. Cross-media issues related to water also need to be considered. Scrubbers for dust removal may also be effective for SO_2 reduction. Wet scrubbing requires pumping energy as well as water and alkali.

Operational data

Dust collection equipment is normally simple to operate and is fully automated.

Applicability

Spray towers have a low pressure drop but are not suitable for removing particles below $10 \mu\text{m}$. Venturi and packed bed washers have been installed for sludge incinerators.

Economics

Operating costs are in the order of EUR 0.5 – 10 per $1\,000 \text{ Nm}^3$ treated flue-gas.

Driving force for implementation

Process gas streams must often be cleaned to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

Some FCC units are equipped with scrubbers.

Reference literature

[168, VROM 1999], [194, Winter 2000].

4.23.4.5 Other wet techniques

Description

Centrifugal washers combine the cyclone principle and an intensive contact with water, like the Venturi washer.

Achieved environmental benefits

Dust emissions can be reduced to 50 mg/Nm³ and below if very large quantities of water are used, such as in an absorber used for a two-stage scrubbing system.

Operational data

Dust collection equipment is normally simple to operate and is fully automated.

Venturi washers need to be operated at sufficient pressure and at full water saturation of the gas phase to reduce the dust emission. For SO₂ removal, scrubbing at pH ± 6 with caustic or lime is necessary.

Applicability

Wash columns, or absorbers with packing are applied in various processes.

Driving force for implementation

Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

Venturi washers are mostly applied for the removal of a combination of dust, acidic components (HCl and HF) at for example cokers and incinerators.

Reference literature

[168, VROM 1999]

4.23.4.6 Combination of particulate abatement techniques

Often a combination of techniques is applied, such as cyclone/ESP, ESP/Venturi/wash column or a cyclone/Venturi/absorber, leading to more than 99 % dust elimination.

4.23.5 Techniques for sulphur recovery and SO₂ abatement

Sulphur is an inherent component of crude oil. Part of this sulphur leaves the refinery in its products, part of it is emitted to the atmosphere (already described in all the processes) and part of it is recovered by some processes located in the refinery for this purpose (more information about the sulphur split in a refinery can be found in Section 1.4.1). Sulphur is an environmental issue that cannot be addressed in an integrated manner if the sulphur associated with the products is not considered. In other words, decreasing emissions from a refinery may result in the production of fuels (products) that may later be burnt in a way that is not environmentally

efficient, thereby jeopardising the environmental effort made by refineries. This is addressed through other types of both European and national legislation.

Because it is such an integrated issue, proper sulphur management should also consider other topics that may not be within the objectives of this document. For example, a global environmental impact assessment of sulphur dioxide emissions should consider the items listed below.

- Atmospheric emissions from processes generating SO_x (furnaces, boilers, FCC, etc.) These issues are in fact included in this document in each of the process sections.
- Atmospheric emissions from sulphur recovery units or of gases containing sulphur in an H₂S form before incineration. This category of sulphur is normally recovered, as shown in Section 4.23.5.2.
- Atmospheric emissions generated by sulphur contained in products for which more stringent specifications already exist, such as gasolines, gas oils, etc. These emissions cannot be considered here because they do not fall within the scope of the IED legislation, but they should be considered as part of an integrated approach.
- Atmospheric emissions generated by products with less stringent specifications (bunkers, coke, heavy fuel oil). Typically, these products (heavy residues) contain high quantities of sulphur. If they are not used in a proper way from an environmental point of view, the emissions can jeopardise the integrated approach to reducing sulphur emissions from the refinery sector. Another threat to this integrated approach is the exporting of these products to countries with less environmental control.
- Sulphur contained in non-fuel products such as bitumen or lubricants is typically not identified as a problem.

In order to reduce the SO₂ emissions at the refinery level, the operator needs to set a global strategy and may have recourse to combinations of the following types of actions:

- selection of fuels and raw materials with low sulphur content, such as:
 - increasing the use of non- or low-sulphur-containing gas (LPG, natural gas, etc.): see Section 4.10 on Energy systems;
 - using low-sulphur crudes (Sections 4.10);
- increase the efficiency of the various abatement techniques, such as:
 - SRU (see Section 4.23.5.2);
 - fuel gas desulphurisation (H₂S reduction with amine treating - see Section 4.23.5.1) or other techniques for FGD (see Section 4.23.5.4 and Sections 4.5.6, FCC units, and 4.10.6, Energy system), gasification (see Section 4.10) or hydrotreatment (see Section 4.13.1).

In this section, only those processes dealing with the recovery of sulphur are considered.

See also Section 4.23.8 for information on the SNO_x combined technique.

4.23.5.1 Amine treating

Description

Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from hydrogen sulphide. This is typically accomplished by dissolving the hydrogen sulphide in a chemical solvent (absorption). Solvents most commonly used are amines. Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide may also be used. In the amine solvent processes, amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulphide is dissolved in the solution. The fuel gases are removed for use as fuel in the process furnaces of other refinery operations. The amine-hydrogen sulphide solution is then heated and steam stripped to remove

the hydrogen sulphide gas. In Figure 4.52, a simplified process flow diagram of an amine treating unit is shown.

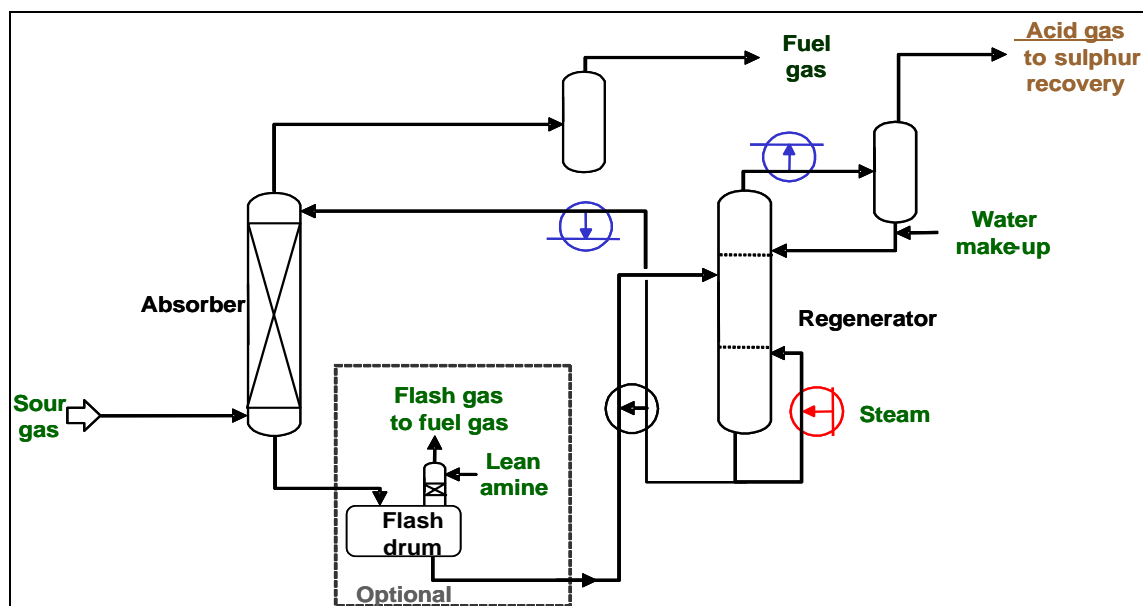


Figure 4.52: Simplified process flow diagram of an amine treating unit

Online analysis of the H_2S content of the RFG leaving the absorber is fed back into the system process control to optimise the performance of the absorber.

The main solvents used are MEA (monoethanolamine), DEA (diethanolamine), DGA (diglycolamine), DIPA (diisopropanolamine), MDEA (methyl diethanolamine) and a number of proprietary formulations comprising mixtures of amines with various additives. One important issue concerning the selection of the type of amine is the selectivity concerning H_2S and CO_2 .

- MEA has had widespread use, as it is inexpensive and highly reactive. However, it is irreversibly degraded by impurities such as COS, CS_2 and O_2 , and therefore is not recommended when gases from cracking units are present.
- DEA is more expensive than MEA but is resistant to degradation by COS and CS_2 and has achieved widespread use.
- DGA is also resistant to degradation by COS and CS_2 but is more expensive than DEA and has the disadvantage of high hydrocarbon solubility into the solution.
- DIPA, which is used in the ADIP process, licensed by Shell. It can be used for selective H_2S removal in the presence of CO_2 and is also effective in removing COS and CS_2 .
- MDEA is nowadays the most widely used, and has a similar characteristic to DIPA, i.e. it has a high selectivity to H_2S , but not to CO_2 . As MDEA is used as a 40 – 50 % solution (activated MDEA) in water, this also has the potential for energy savings. Because of the low selectivity for CO_2 absorption, DIPA and MDEA are very suitable for use in Claus tail gas amine absorbers, as these do not tend to recycle CO_2 over the Claus unit. MDEA is applied as a single solvent or as in proprietary formulation mixtures.

Achieved environmental benefits

Sulphur is removed from a number of refinery process off-gas streams (sour gas or acid gas) in order to meet the SO_x emission limits of the applicable regulation and to recover saleable elemental sulphur. The amine treating unit produces two streams for further use/processing in downstream units:

- the treated gas stream with a residual H_2S content normally in the ranges displayed in Table 4.80; and

- the concentrated H₂S/acid gas stream, which is routed to the SRU for sulphur recovery (discussed in Section 4.23.5.2).

Table 4.80: Residual H₂S concentration achievable in the refinery fuel gas

| Typical amine scrubbing pressure (absolute bar) | Residual H ₂ S concentration (mg/Nm ³) |
|---|--|
| 3.5 | 20 – 220 |
| 20 | 4 – 40 |
| 50 | 2 – 15 |
| <i>Source: CONCAWE 4/09 report. Daily average values.</i> | |

Cross-media effects

They are summarised in Table 4.81. Energy consumption must also be considered (see above).

Table 4.81: Overview of the cross-media effects related to some aspects of amine treating

| | Source | Flow | Composition | Comments |
|---|---|---|---|--|
| Effluent: amine blowdown | Amine regenerator | 10 – 50 t/yr for a 5 Mt/yr refinery | Decomposed amine up to 50 % in water | In order not to disturb the biotreater operation and to meet effluent discharge specifications on N-Kj, a storage tank or production planning can be used to control very small flows to the WWTP. The WWTP microbiology requires acclimatisation time to be able to biodegrade amines - MDEA requires several days, for MEA it is shorter. |
| Waste 1: | Amine filter cleaning residue | Plant-specific | FeS and salt deposits | Removed by a skid-mounted unit operated by a specialised contractor (usually the filter supplier) |
| Waste 2: | Saturated activated carbon from skid- mounted unit | Plant-specific | Decomposition products, heavy ends and amine emulsions | The saturated activated carbon filling has to be replaced occasionally for disposal or regeneration |

Operational data

The use of selective amines should be considered, e.g. for a stream containing carbon dioxide. Measures should be taken to minimise hydrocarbons entering the sulphur recovery system; the operation of regenerator feed drums should be controlled to prevent hydrocarbon accumulation in, and sudden release from, the amine regenerator, as this is likely to lead to an emergency shutdown of the SRU.

Utility consumption per tonne of H₂S removed in an amine treating unit is approximately as follows:

| Electricity (kWh/t) | Steam consumed (kg/t) | Cooling water (m ³ /t, ΔT = 10 °C) |
|------------------------|--------------------------|--|
| 70 – 80 | 1 500 – 3 000 | 25 – 35 |

Usually a fresh solvent make-up rate of 10 – 50 t/yr is required to maintain solvent strength for a 5 Mt/yr refinery.

Amine solutions should be reused wherever possible and, where necessary, suitably treated before being properly disposed of. Recycling of monoethanolamine solutions: corrosive salts, which concentrate during recycling, can be removed via ion exchange or thermal reclaiming techniques. Some proprietary solutions may be biodegradable under suitable conditions.

It is also important that the amine processes have sufficient capacity to allow for maintenance activities and upsets. This sufficient capacity can be achieved by having redundancy equipment, or by applying load-shedding, emergency amine scrubbers or multiple-scrubber systems.

Applicability

Process off-gas streams from the coker, catalytic cracking units, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulphide mixed with light refinery fuel gases. Additional treatment, such as COS converter, is necessary to ensure appropriate sulphur removal in off-gas from cokers (see Section 4.7.8.4). Emergency H₂S scrubbers are also important.

Economics

The cost of upgrading the refinery amine treatment system (2 %) to meet 0.01 – 0.02 % v/v of H₂S in fuel gas is around EUR 3.75 – 4.5 million. This cost is battery limit costs based on 1 998 prices and includes items such as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact. In some cases, these factors might be expected to increase the costs by some 50 %.

Driving force for implementation

To reduce the sulphur content of flue-gases.

Example plant(s)

Common technique used all over the world.

Reference literature

[148, Irish EPA 1993], [168, VROM 1999], [182, Ecker 1999], [207, TWG 2001].

4.23.5.2 Sulphur recovery units (SRU)

H₂S-rich gas streams from amine treating units (see Section 4.23.5.1) and sour water strippers (see Section 4.24.2) are treated in a sulphur recovery unit (SRU), which most often consists of a Claus process for bulk sulphur removal and subsequently a tail gas treatment unit (TGTU) for the remaining H₂S removal. Other components entering the SRU may include NH₃, CO₂ and, to a minor extent, various hydrocarbons.

4.23.5.2.1 Increased efficiency of the Claus process

Description

The Claus process consists of the partial combustion of the hydrogen sulphide-rich gas stream (with one-third of the stoichiometric quantity of air) and then reacting the resulting sulphur dioxide and unburnt hydrogen sulphide in the presence of an activated alumina catalyst to produce elemental sulphur. As shown in Figure 4.53, the Claus unit then consists of a reaction furnace followed by a series of converters and condensers, where:

- the partial combustion and a part of the sulphur formation ($2\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_2 + \text{S} + 2\text{H}_2\text{O}$) occurs in the primary reactor;
- the main Claus reaction for sulphur formation ($2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$) takes place in the different catalytic converters;
- and liquid elementary sulphur is collected from the various condensers in a common pit, as shown in Figure 4.53.

Side reaction effects also occur that produce carbonyl sulphide (COS) and carbon disulphide (CS_2), which have raised problems in many Claus plant operations because they cannot be easily converted to elemental sulphur and carbon dioxide.

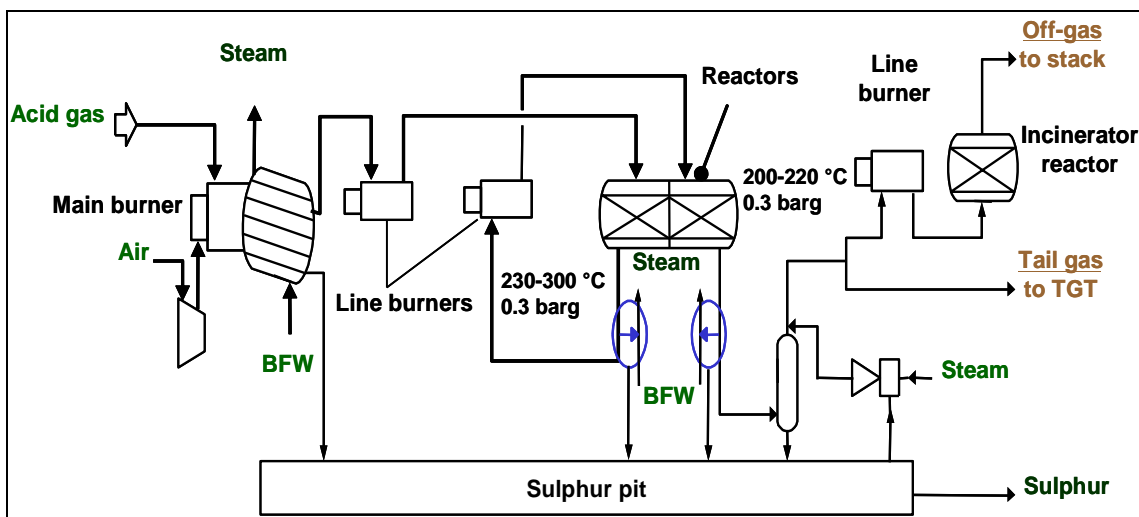


Figure 4.53: Simplified process flow diagram of a sulphur recovery unit (Claus process)

The overall capacity of the Claus plants can be increased with the use of oxygen enrichment technologies (e.g. with the OxyClaus process). However, this has not had any beneficial effect in the sulphur recovery efficiency of the Claus plant. The use of this process can increase the unit capacity up to 200 % in existing Claus sulphur recovery units, or can be an option for a more economical design for new Claus sulphur units.

The techniques given below can be used and retrofitted to existing SRUs for increasing the Claus process efficiency.

- An improved unique burner system and enhanced combustion conditions to reach a minimum temperature of 1 350 °C, which allows a better destruction of ammonia and mercaptans in the combustion chamber, and a reduction of the Claus catalytic bed plugging by ammonium salts [Questionnaire n° 31].
- High-performance catalysts process (e.g. Selectox), which can be used in combination with the first stage of the Claus unit to promote the oxidation of H_2S to SO_2 without the use of a flame. They allow for a significant increase in the sulphur recovery efficiency.
- An automated control of the air feed to the Claus reaction furnace optimises sulphur recovery.

Achieved environmental benefits

The SRU is characterised by its sulphur recovery efficiency, calculated as the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits. This fraction includes the dissolved H_2S (typically 200 – 500 ppm weight) which must be removed from the liquid sulphur at a later stage of the process (see Section 4.23.5.2.4 on sulphur degassing).

The sulphur recovery efficiency of a SRU closely depends on the number of Claus reactors that are operated in series in the sulphur recovery unit chain, as shown in Table 4.82.

Table 4.82: Sulphur recovery efficiency of Claus process SRUs in European sites

| Number of Claus reactors | Number of data-sets | Sulphur recovery efficiency (% H ₂ S converted) | | |
|--------------------------|---------------------|--|--------|-----------|
| | | Observed range | Median | Typical |
| 1 | NA | NA | NA | 90 |
| 2 | 87 | 92.4 – 97.8 | 96.1 | 95 – 96.5 |
| 3 | 27 | 96.0 – 98.4 | 97.0 | 96.5 – 98 |

Sources: [36, CONCAWE n°4/09 2009]

Most recent or recently refurbished units have three- to four-stage units (including SuperClaus), meaning that they have three to four sets of converters and condensers.

Furthermore, state-of-the-art oxidation catalysts (e.g. Selectox or Criterion – these types of catalysts are suitable for promoting the Claus reaction) have been used in North American refineries with significant increased efficiency rates reported [25, Pham et al.2009], specifically:

- from 90 to 97 %; at first Claus stage level;
- from 96 – 97 % to 99.8 – 99.9 %; for a full three-stage Claus unit followed by a tail gas treating unit that reduces sulphur components to H₂S and recovers H₂S with amine treating. [261, Criterion 2006].

Cross-media effects

The reduction of SO₂ leads to an increase of the CO₂ emission. For example, for a 100 t/d sulphur Claus plant, the application of three reactors would lead to an emission of 4.8 tonnes of sulphur per day at a cost of 8.5 tonnes of CO₂ per day. Table 4.83 shows indicative estimates of the incremental emission of CO₂ which will be associated with the marginal incremental reduction of SO₂ achieved for various SRU+TGTU configurations. It is assumed that the low-pressure steam generated on the SRU can be fully valorised as energy, which goes against the amine-based TGTU, but this does not necessarily reflect real case situations.

Table 4.83: CO₂ incremental emissions for the main categories of SRU+TGTU techniques

| SRU technology | Incremental t CO ₂ per incremental t SO ₂ reduced (compared to a base two-stage Claus ⁽¹⁾) |
|---------------------------------------|--|
| Two-stage Claus + 3rd stage Claus | 0.25 |
| Two-stage Claus + SuperClaus | 0.25 |
| Two-stage Claus + Catalytic Oxidation | 0.31 |
| Two-stage Claus + sub-dew point TGCU | 0.55 |
| Two-stage Claus + amine-based TGCU | 0.75 |

⁽¹⁾ Based on a 100 t/d SRU fed with 80 % acid gas feed (95 % H₂S) and 20 % gas from the sour water stripper (56 % H₂S, 43 % NH₃).

Operational data

- Feed/air ratio control, temperature control of the furnace, reactors and condensers and good demisting of liquid sulphur, especially from the final condenser exit gas stream, are important parameters in achieving maximum sulphur recovery. Good control and availability is crucial as a technique, to deliver any design targets. In this line, the use of state-of-the-art control and monitoring systems can be seen as an important technique.

Use of a tail gas analyser linked to the process control system (feedback control) will aid optimum conversion during all plant operating conditions, including changes to sulphur throughput.

- To have a SRU configuration with sufficient capacity for the H₂S feed to the unit including the sourest crude oil to be used is important. The duplication of the SRU capacity is important to consider to obtain low sulphur emissions. This should also be large enough to allow the scheduled maintenance activity to proceed every two years, without a significant increase of sulphur emissions.
- To have utilisation factors close to 100 % increases how efficiently the units are used. These capacity factors must also include the impact of major turnaround maintenance.
- Use a good furnace burning-zone design and effective furnace temperature and oxygen control systems where sour water stripper off-gases are a feed stream, because the process must also be designed and operated to complete the destruction of ammonia. Ammonia breakthrough may lead to deposition and blockages of catalyst beds by ammonium salts (e.g. carbonate/sulphate) and these SRUs need to be monitored for avoidance of this.

Typical emissions and utilities necessary for a 20 000 t/yr SRU are summarised in Table 4.84 and Table 4.85.

Table 4.84: Typical emissions of a 20 000 t/yr SRU

| Type | Source | Flow | Composition min/max | Comments |
|---|--|---|---|---|
| Air emissions: CO ₂ SO ₂ NO _x | Incinerator off-gas | 0.2 % of the total H ₂ S load to the SRU | SO ₂ : 1 500 mg/Nm ³ Through presence of NH ₃ , non-catalytic DeNO _x ing takes place | Amount of SO ₂ released depends on total sulphur production and overall sulphur recovery or conversion |
| Liquid effluents: | Knockout drum for water in SWS off-gas | 0.02 m ³ /h | H ₂ S: 50 mg/l; Phenol: 100 mg/l; NH ₃ : 2 000 mg/l | To be treated in the SWS |
| Solid waste: | Spent SRU catalyst | Plant-specific | Mainly Al ₂ O ₃ , depending on the catalyst composition | |

Table 4.85: Typical utility consumption

| Fuel (MJ/t) | Electricity (kWh/t) | Steam produced (kg/t) | Cooling water (m ³ /t, ΔT=10 °C) |
|---------------|---------------------|-----------------------|---|
| 1 000 – 1 600 | 60 – 75 | 1 500 – 2 000 | 0 – 20 |

In some cases, the SRU needs a pilot flame to co-fire natural or fuel gas when the H₂S concentration is so low that a stable flame cannot be achieved.

Applicability

Fully applicable. The oxygen enrichment technologies (e.g. the OxyClaus process) increase the plant flexibility, as they allow the treatment of feed gases for a wide H₂S content range of 20 – 100 % v/v. Temporary higher, lower or fluctuating amounts of hydrogen sulphide can be handled by automatic changeover from air to oxygen operation and vice versa. Higher hydrocarbon contents can also be processed, and an almost complete combustion of the ammonia contained in sour water stripper off-gases achieved, provided the reaction furnace temperature is above 1 350 °C, there is adequate residence time, and a properly designed burner.

Economics

Table 4.86: Cost examples of two typical upgrade projects for an existing two-stage 100 t/d SRU

| Upgrading project | Plant size range | Approximate capital cost (EUR million installed) | Approximate operating cost per year (EUR million) |
|--|------------------|--|---|
| Upgrade SRU with O ₂ enrichment to increase throughput from 100 t/d to 170 t/d ⁽¹⁾ | 100 t/d | 2.1 – 5.3 | 1.6 (oxygen consumption) |
| Addition of a 3rd stage Claus reactor ⁽²⁾ | 100 t/d | 2.0 – 3.0 | 0.1 |

⁽¹⁾ There are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact. In some cases, these factors might be expected to increase the costs by some 50 %.

⁽²⁾ Capacity of the process: 30 000 t/yr of sulphur production. Volume of gas to be treated: 60 million m³/yr. Pollutant initial concentration: 34 000 mg SO₂/m³ (1.2 % molar or 2.3 % w/w, the rest considered as air) – 1998 prices.

See also Table 4.94 for additional information on costs related to SRUs.

Driving force for implementation

To reduce sulphur emissions.

Example plants

In the market, more than five licensors of this process exist. The Claus process is widely applied in the refinery sector. The two-stage Claus process is the most common in Europe. More than 35 oxygen-enriched (OxyClaus) systems (4 – 270 t/day) are in operation around the world.

Reference literature

[25, Pham et al.2009], [36, CONCAWE n°4/09 2009], [151, Sema, Sofres 1991], [165, Ademe 1999], [166, CONCAWE 1999], [183, HP 1998], [194, Winter 2000], [201, Manduzio 2000], [261, Criterion 2006].

4.23.5.2.2 Tail gas treatment units (TGTUs)**Description**

Current methods for removing sulphur from the hydrogen sulphide gas streams are typically a combination of two processes: the Claus process (see Section 4.24.5.2.1) followed by a tail gas clean-up or treatment unit (TGTU). Since the Claus process by itself removes only about 94 – 96 % (two stages) or 96 – 98 % (three stages) of the hydrogen sulphide in the gas stream, the TGTU processes must be used to further recover sulphur.

A large number of processes for TGTUs have been developed in order to enhance the recovery of sulphur compounds from natural gas and/or refinery sources. The most frequently operated TGTU processes (see Figure 3.36 in Section 3.23.2) can be broadly divided into the following four categories according to the principles applied:

- direct oxidation to sulphur,
- continuation of the Claus reaction,
- reduction to H₂S and recovering sulphur from this H₂S,
- oxidation to SO₂ and recovering sulphur from SO₂.

4.23.5.2.2.1 Direct oxidation to sulphur

In these processes, the main step is achieved on a solid catalyst. In particular:

- **PROClas** stands for Parson RedO_x Claus. It is a dry catalytic process that contains three additional stages (one reduction and two oxidations). In the first stage, a highly selective catalyst developed by the US Lawrence Berkeley National Laboratory is used for the reduction of SO₂ to elemental sulphur. In the second stage, the remaining H₂S is then oxidised to also form elemental sulphur under the presence of another highly specialised catalyst. The remainder is sent to a thermal oxidiser.
- The **SUPERCLAUS** process is by far the most commonly used in this category. It is based on two principles: i) operating the Claus plant with excess H₂S to minimise the SO₂ content in the Claus tail gas, and to simplify and make the air ratio control more flexible, and ii) oxidising selectively the remaining H₂S in the Claus tail gas by means of a specific catalyst, which efficiently converts the remaining H₂S in the presence of water vapour and excess oxygen into elemental sulphur only. This reaction takes place in a specific converter (an oxidation reactor), downstream of two or three reactors in the traditional Claus unit. The catalyst used is an alumina-based catalyst coated with iron oxide and chromium oxide layers.

4.23.5.2.2.2 Continuation of the Claus reaction

These processes operate over a bed of standard Claus catalysts or a non-volatile organic solvent under sub-dew point conditions in the liquid phase. In particular:

- The **CBA** (cold bed absorption) process is very similar to the Sulfreen process except in the fact that the CBA process uses a hot process stream indigenous to the Claus process to accomplish regeneration of the sulphur-loaded catalyst bed. The hot process stream is part of the effluent of the first Claus reactor. Several configurations are available depending on the number of Claus converters.
- The **CLAUSPOL** is a process where the tail gas is put into contact with a solvent (polyethylene glycol) and the reaction of H₂S and SO₂ is catalysed by a dissolved catalyst (sodium salt of an inorganic acid, e.g. sodium salicylate), which is a solvent for H₂S and SO₂, but not for liquid sulphur. The Claus reaction can therefore proceed at low temperatures (120 °C) and is shifted further to the right as the produced sulphur is removed from the reaction medium, as it is not soluble and separates.
- The **SULFREEN** process is a dry-bed, sub-dew point absorption process based on the extension of the Claus reaction, i.e. catalytic oxidation of H₂S to S. This basically consists of two (occasionally three for large capacities) Sulfreen reactors in series with the Claus reactors. Activated alumina is used as a catalyst. Regeneration is needed since the sulphur accumulates on the catalyst decreasing its activity. Sulphur from the hot regeneration stream is condensed in a dedicated condenser. Several variations are used.
 - The **HydroSulfreen** adds a conversion step upstream of the first sulfreen reactor, to perform the hydrolysis of COS and CS₂ to H₂S with the help of an activated titanium oxide Claus catalyst in order to adjust the H₂S/SO₂ ratio more precisely. The Claus reaction takes place in the HydroSulfreen reactor and sulphur produced is condensed in a dedicated condenser.
 - The **DoxoSulfreen** concept is based on two ideas: the upstream units are operated to get a slight excess of H₂S, compared to the quantity necessary to maintain the Claus ratio, therefore a near total SO₂ conversion takes place on the conventional Sulfreen catalyst; then the remaining H₂S is directly oxidised to elemental sulphur.

- The **MAXISULF** is a simplified sulfreen process, including basically a single-stage (one absorber, one regenerator) unit with an open regeneration loop. The regeneration gas is fed to the absorber together with the Claus tail gas.

4.23.5.2.2.3 Reduction to H₂S and recovering sulphur from H₂S

The recovery of sulphur can be carried out with amine scrubbing processes for recycling to the upstream Claus unit. In particular:

- The **FLEXSORB** process has been developed by Exxon Mobil as an alternative to the MDEA amine treatment process. A specific solution is used to remove H₂S from the tail gas after conversion of sulphur compounds to H₂S has been performed. The absorbed H₂S is recycled back to the Claus plant for sulphur recovery.
- The **HCR** (High Claus Ratio) process is directly derived from the SCOT and designed by Siirtec Nigi.
- The **RAR** (Reduction, absorption, recycle) process is a MDEA reductive treatment allowing the use of plain MDEA or specifically formulated MDEA-based solutions. It was originally designed for Claus tail gas treatment, but can also be applied to other, more complex, hydrogen sulphide-containing gas streams which are either too diluted or too contaminated for direct processing through normal Claus units.
- The **SCOT** (H₂S Scrubbing) process is by far the most widely applied in this category. SCOT stands for Shell Claus off-gas treatment. As shown in Figure 4.54, the concepts underlying H₂S scrubbing processes are:
 - hydrogenation and hydrolysis of all sulphur compounds to H₂S passing it through a cobalt-molybdenum catalyst at 300 °C with the addition of a reducing gas;
 - absorption of H₂S by an amine solution (generic amine or specialty amine);
 - regeneration of the amine solution and recycling of the H₂S to the upfront Claus reaction furnace.
- The **BSR** (Beavon Sulphur Removal) process family where, in a first step, sulphur compounds are catalytically (cobalt-molybdate based) converted into H₂S through a hydrogenation/hydrolysis reaction at high temperature (300 – 400 °C). In a second step, H₂S is removed by a chemical solution (e.g. amines process) or another tail gas process.

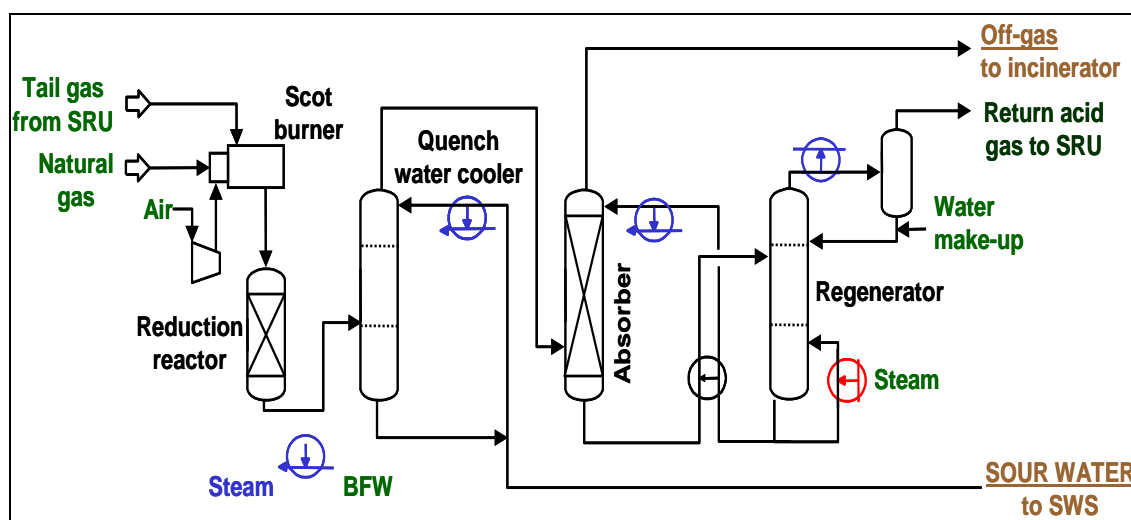


Figure 4.54: Simplified process flow diagram of a tail gas SCOT unit

The recovery of sulphur can be carried out with other recovery processes such as the following:

- The **LO-CAT** process is a liquid redox system that uses a chelated iron solution to convert H_2S . Absorption and regeneration are performed in a single vessel divided into two sections: the centerwell and the outer space where aeration with air is performed. The purpose of the centerwell is to separate the sulphite ions from air in order to minimise by-product formation (e.g. thiosulphate). The difference in aeration (and therefore of density) between the centerwell and the outer space gives sufficient driving force for solution circulation between the absorption and the regeneration zones without the need for a specific pump. The last type of processing scheme is called the ‘aerobic unit’ and is used to treat air contaminated with H_2S . All reactions take place in the same vessel, at the expense of increased by-product formation, but with the advantage of a reduced capital cost.
- **MODOP** or **BSR/SELECTOX** processes use direct oxidation after reduction to H_2S .

4.23.5.2.2.4 Oxidation to SO_2 and recovery of sulphur from SO_2

The processes used one of the following (for more details, see also Section 4.23.5.4 on Sulphur dioxide abatement techniques):

- The **WELLMAN-LORD** process, where sodium sulphite reacts with SO_2 in the flue-gases, forming sodium bisulphite. The concentrated solution is collected and evaporated for regeneration. In the regeneration step, using steam, the sodium bisulphite is broken down, to release the sodium sulphite, to be recycled back to the flue-gases.
- The **CLINTOX** process, where the sulphur species are burnt to be converted to SO_2 , which is then absorbed in a physical solvent, stripped from the solvent and returned to the Claus plant to replace oxygen in the air and contribute to increase the sulphur capacity of the Claus furnace unit.
- The **LABSORB** process, based on an absorption/regeneration cycle including the use of an absorbing solution containing caustic soda and phosphoric acid to capture SO_2 as sodium bisulphite.

Achieved environmental benefits

Tail gas treatment units increase the overall recovery of H_2S and decrease the sulphur emissions from the refinery. For example, if a refinery has a 100 t/d SRU, with a two-stage Claus reactor, this SRU will emit around 5 t/d (1 750 t/yr) of sulphur, and will most likely be one of the major SO_2 emission sources of the site. If a tail gas clean-up process is included in such a refinery, the emissions of sulphur may be reduced to 0.5 t/d, representing a reduction of 90 % of the sulphur emissions from the sulphur recovery units, and saving 1 575 t/yr of SO_2 .

Table 4.87 shows the expected overall sulphur recovery yield, the resulting additional recovered sulphur and the dry basis sulphur emission (in the form of SO_2 species) after incineration, of a selection of the tail gas treatments considered in this section.

Table 4.87: Expected performances of SRU for various TGTU processes and configurations

| For a generic 100 t/day SRU initially equipped with a two-stage Claus: | Expected sulphur recovery efficiency ⁽¹⁾ | Expected additional sulphur recovered ⁽²⁾ | Indicative SO ₂ concentration after incineration step (3 % O ₂ content - dry basis) ⁽³⁾ |
|--|---|--|--|
| Added process: | (%) | t/d | mg/Nm ³ |
| Base (two-stage Claus) | 95 – 96 | - | 31 000 – 38 000 |
| + 3rd stage Claus | 96 – 98 | 1.00 – 2.00 | 16 000 – 31 000 |
| + 3rd stage Claus and Selectox | 97 | NA | 24 000 |
| I. Direct oxidation to sulphur | | | |
| + PROClas | 99.5 | 4.10 | 4 000 |
| + SuperClaus | 98 – 99.3 ⁽⁴⁾ | 2.77 | 5 700 – 16 000 |
| II. Continuation of Claus reaction/Sub-dew point | | | |
| + CBA (cold bed absorption) | 99.3 – 99.4 | 3.65 | 5 000 – 5 700 |
| + Clauspol ⁽⁵⁾ | 99.5 – 99.9 | | 800 – 4 000 |
| + Clauspol II ⁽⁶⁾ | 99 – 99.8 | 3.75 | 1 600 – 8 100 |
| + Sulfreen | 99 – 99.2 | 3.56 | 6 500 – 8 100 |
| + 3 rd stage Claus + Sulfreen | 99.2 – 99.5 | | 4 100 – 6 500 |
| + DoxoSulfreen ⁽⁷⁾ | 99.8 – 99.9 | 4.04 | 800 – 1 600 |
| + HydroSulfreen ⁽⁸⁾ | 99.5 – 99.7 | | 2 500 – 4 100 |
| + Maxisulf | 98.5 | | 12 500 |
| + 3 rd stage Claus + Maxisulf | 99.0 – 99.5 | | 4 000 – 8 100 |
| III. Reduction to H₂S and S recovery from H₂S | | | |
| + Flexsorb | 99.9 | 4.10 | 800 |
| + RAR | 99.9 | 4.10 | 800 |
| + SCOT (amine-based process) | 99.5 – 99.95 | NA | 400 – 4 100 ⁽¹⁰⁾ |
| + LO-CAT II ⁽⁹⁾ | 99.99 | 4.16 | 90 ⁽¹⁰⁾ |
| + Beavon (BSR) | 99.5 – 99.9 | NA | 800 – 4 100 ⁽¹⁰⁾ |
| IV. SO₂ abatement | | | |
| Scrubbing techniques | 99.9 | | 800 ⁽¹⁰⁾ |
| Main source for sulphur recovery efficiency: [131, Ballaguet et al.2006], [76, Hydrocarbon processing 2011] | | | |
| ⁽¹⁾ For the whole treatment train (SRU + TGTU). | | | |
| ⁽²⁾ From the TGTU step only. | | | |
| ⁽³⁾ Using the calculation described in Annex 8.6, Appendix B: SO ₂ concentration after the incineration step is dependent on the fuel gas/acid gas ratio (FG/AG is specific to SRU configuration and operating parameter). For illustration, the calculation has been made for a FG/AG ratio of 4 %. | | | |
| ⁽⁴⁾ Values from provider. Upper level is the maximum value guaranteed. | | | |
| ⁽⁵⁾ See present section under applicability information. | | | |
| ⁽⁶⁾ Upper level requires COS and CS ₂ to be hydrolysed down to 300 ppmv of S through the catalytic stage. | | | |
| ⁽⁷⁾ Sulfreen reactors, hydrolysis section and DoxoSulfreen reactors. | | | |
| ⁽⁸⁾ Sulfreen reactors and hydrolysis section. | | | |
| ⁽⁹⁾ As LO-CAT II tail gas cannot be incinerated, sulphur is in the form of H ₂ S species. | | | |
| ⁽¹⁰⁾ Incineration step may not be systematically required for this technique. | | | |

Cross-media effects

As already mentioned, the reduction of SO₂ leads to an increase in the CO₂ emissions (see Table 4.83 in Section 4.23.5.2.1). For instance, the application of a tail gas treatment would lead to a SO₂ reduction of 96 % (if compared with the three-reactor option), however at an increase in CO₂ of 110 %. For example, for a 100 t/d sulphur Claus plant with three reactors, the application of a TGTU would reduce emissions of SO₂ to 0.1 t/d, but at a price of increasing the CO₂ emissions to 18 t/d.

Table 4.88: Cross-media effects associated with some of the TGTU

| Emissions based on 20 000 t/yr SRU/TGCU | | | | |
|---|---|--|--|--|
| | Source | Flow | Composition min/max | Comments |
| Effluents | Sour water from quench column for SRU off-gas | 1 m ³ /tonne S produced (2 m ³ /h) | H ₂ S: 50 mg/l; Phenol: 100 mg/l; NH ₃ : 2 000 mg/l | To be treated in the SWS |
| Waste: SCOT | Spent TGTU catalyst | Regeneration and disposal 20 – 100 t/yr | 2 – 8 % Ni/Mo on Al ₂ O ₃ , S: 5 – 15 %; Coke: 10 – 30 % | Spent Claus catalyst is pyrophoric and needs purging with N ₂ |

Operational data

The actual sulphur recovery yield from the SRU associated with its TGTU depends on the feed composition, the catalyst run time (for catalytic oxidation TGTU), and the progressive fouling during the operation run. Table 4.89 is based on actual sulphur recovery measurements taken in more than 40 European refineries between 2004 and 2008. Measurement campaigns have been carried out during a limited period of time (1 – 2 days) at various given times in the catalyst cycle, thus reflecting a wide range of unit operating conditions and catalyst lifetime situations.

Table 4.89: Expected range of recovery efficiencies for main TGTU categories

| TGTU categories | Number of data-sets | % Recovery efficiency (% H ₂ S converted) as daily average for the whole SRU+TGTU | | |
|----------------------------|---------------------|--|--------|--------------|
| | | Observed range | Median | Typical |
| Catalytic direct oxidation | 26 | 95.5 – 99.3 | 98.5 | 98 – 99 |
| Sub-dew point | 16 | 98.0 – 99.8 | 99.4 | 99 – 99.5 |
| Amine-based | 19 | 98.7 – 99.99 | 99.9 | 99.5 – 99.95 |
| <i>Source: CONCAWE</i> | | | | |

Another set of site data recovery efficiencies for eight SRUs from five German refineries is shown in Table 4.90.

Table 4.90: Range of sulphur recovery measured after TGTU in 5 German refineries

| Refinery/ installation number | TGTU process | Sulphur capacity (t/d) | Operating grade (t/d) | Measured % recovery efficiency ⁽¹⁾ |
|--|--------------|------------------------|-----------------------|---|
| Ref 2 –Claus 1 | Incineration | 34.7 | 18.1 | 98 |
| Ref 3 –Claus 1 | Incineration | 16 | NA | 98 |
| Ref 3 –Claus 2 | Incineration | 17 | NA | 98 |
| Ref 1 –Claus 1 | Sulfreen | 55 | 26.4 | 99.6 |
| Ref 4 –Claus | Sulfreen | 69.9 | 55.2 | 99.5 |
| Ref 1 –Claus 2 | SCOT | 170 | NA | 99.9 |
| Ref 5 –Claus | SCOT | 128.6 | 80 | 99.7 |
| Ref 2 –Claus 2 | Clauspol II | 33.6 | 10.2 | 98.8 |
| ⁽¹⁾ Estimated as efficiency = 1-SER (sulphur emission ratio). Daily average. NA: not available. <i>Source: TWG 2010-DE</i> | | | | |

Applicability

TGTUs are applicable to both new and existing plants. Capacities range from 2 tonnes to more than 2 000 tonnes of sulphur per day from the combined Claus/tail gas treatment units. However, the space occupied by such units can be significant. As an example, a new TGT unit (540 t/day gas treatment capacity – 10 t/day sulphur recovery) including a third Claus stage and a Sulfreen Maxisulf TGT was built in 2008 on a French site and occupies an area of 960 m².

Significant difficulties have been reported concerning the poor utilisation factor of two Clauspol units (0 – 25 %), due to side reactions favouring the formation of sodium salt precipitates and highly corrosive components (native SO_3 and NH_4HSO_4). Furthermore, shutdowns for cleaning and maintenance generate large quantities of heavily polluted waste waters contaminated with sulphur and PEG (DCO 200 g/l).

Economics

Table 4.91 gives estimates of costs for a new SRU or for the upgrading of an existing SRU, depending on the sulphur recovery yield target and the treatment capacity, while Table 4.92 shows a relative capital cost comparison for the main categories of TGT options in relation to a two-stage Claus base case.

Table 4.91: Cost examples for new SRUs and SRU upgrading versus treatment capacity

| Recovery yield objective | Plant size range | Approximate capital cost (EUR million installed) | Approximate operating cost (EUR per year) |
|--|------------------------------|--|---|
| Additional 3rd stage Claus + TGTU (Maxisulf) to give >98.5 % | 540 t/d | 31 (2008) | NA |
| New Sulfreen TGT (Sulfreen) on existing SRU to give 99.5 % | 175 t/d | 18 (2006) | NA |
| Additional 3rd stage Claus + TGTU (Superclaus) to give >98.5 % | 210 t/d | 26 (2005) | 600 000 (2005) |
| New SRU including TGTU to give >99 % S recovery (1998) | 50 t/d 100 t/d 250 t/d | 12 19 35 | NA |
| Tail gas treatment unit to improve existing SRU recovery to 99 % (1998) | 50 t/d 100 t/d 250 t/d | 1.6 2.1 2.9 | NA |
| Tail gas treatment unit to improve SRU existing recovery to 99.8 % (1998) | 50 t/d 100 t/d 250 t/d | 3.5 4.4 6.3 | NA |
| There are battery limit costs including equipment, licencing fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact. In some cases these factors might increase the costs by some 50 %. | | | |

Table 4.92: Relative capital cost for the upgrading of an existing 100 t/d SRU

| SRU upgrading technology option | Relative capital cost in 2009 ⁽¹⁾ |
|---|--|
| Two-stage Claus | 100 |
| Two-stage Claus + 3rd stage Claus | 109 |
| Two-stage Claus + sub-dew point TGT (e.g. CBA) | 120 |
| Two-stage Claus + catalytic direct oxidation TGT (e.g. SuperClaus) | 130 |
| Two-stage Claus + advanced Sulfreen TGT | 140 |
| Two-stage Claus + amine-based TGT | 194 |
| ⁽¹⁾ Based on a 100 t/d SRU fed with 80 % acid gas feed (95 % H_2S) and 20 % gas from the sour water stripper (56 % H_2S , 43 % NH_3). | |

The reference to the upstream sulphur unit is indicative and corresponds to the way this kind of comparison is usually presented in the literature. This comparison should be taken with care when comparing with other studies, as the capital cost of a sulphur unit may fluctuate +/- 30 %.

Examples of cost-effectiveness for the upgrading of different types of Claus plant with various techniques are shown in Table 4.94.

Operating costs for two Hydrosulfreen units of total maximum capacity 15.2 t/h (44 000 Nm³/h) are estimated in Table 4.93. Costs are given for a utilisation factor of 82 % for each unit.

Table 4.93: Detailed operating costs of a Hydrosulfreen TGT unit

| | Consumption | Cost (EUR/h) |
|---|---------------------------------|---------------------|
| Catalyst and utility consumption | | |
| Catalysts and activated carbon | 5-year lifetime basis (assumed) | 9.13 |
| Fuel gas to incinerator | 0.68 t/h | 222.4 |
| Combustion air to incinerator | 17.32 t/h | 10.8 |
| LP Steam | 0.70 t/h | 11.5 |
| Boiler feed water | 8.81 t/h | 26.4 |
| Air + nitrogen | 50 + 25 m ³ /h | 1.7 |
| Electricity | 330 kW installed | 12.4 |
| | Total: | 294.33 |
| Utility production | | |
| MP Steam production | 8.39 t/h | -143.7 |
| LLP Steam production | 2.90 t/h | -41.8 |
| | Total: | -185.5 |
| | Net cost: | 109 |

Table 4.94: Economics of three SO₂ abatement techniques in sulphur recovery units – Cost-effectiveness data from a sample of 7 SRUs

| | | | | | | | Direct oxidation to sulphur (e.g. SuperClaus process) | | | | | Sub-dew point (e.g. Sulfreeen process) | | | | |
|--------------------------------------|------------------------|-------------------------------------|--------------------------------|------------------------------------|---------------------------------------|-----------------------|---|-------------------------------------|--------------------------------|---------------------------------|------------------------------------|--|-------------------------------------|--------------------------------|------------------------------------|---|
| | | | | | | | Efficiency | ACC | Fixed OP | Variable OP | S market value €/t S | Efficiency | ACC | Fixed OP | Variable OP | |
| Base case in 2006 - Claus process | | | | | | | 99 % | 7.4 % | 4 % TEC/yr | 3.9 €/t S | 160 | 99.5 % | 7.4 % | 4 % TEC/yr | 2.8 €/tFF | |
| Unit | Number parallel trains | Design S | Utilisation | Actual S | Incinerator t/yr | S recovery efficiency | S recovery efficiency | SO ₂ removed (From Base) | Total erected Cost (From Base) | Annualised Cost: Base to SClaus | Cost-Effectiveness: Base to SClaus | S recovery efficiency | SO ₂ removed (From Base) | Total erected Cost (From Base) | Annualised Cost: Base to Sulfreeen | Cost-Effectiveness: SClaus to Sulfreeen |
| | | t/yr | % | t/yr | t/yr | % | % | t/yr | M€ | k€/yr | €/t SO ₂ | % | t/yr | M€ | k€/yr | €/t SO ₂ |
| 1 | 2 | 150 380 | 58 % | 87 833 | 1 313 | 98.5 % | 99 % | 843 | 26.1 | 3 243 | 346 | 99.5 % | 1 734 | 65.2 | 7 539 | 4 819 |
| 2 | 1 | 36 500 | 43 % | 15 604 | 566 | 96.5 % | 99 % | 808 | 8.4 | 959 | 1 185 | 99.5 % | 970 | 21.1 | 2 374 | 8 754 |
| 3 | 1 | 36 865 | 38 % | 14 186 | 233 | 98.4 % | 99 % | 176 | 8.5 | 1 009 | 5 715 | 99.5 % | 320 | 21.2 | 2 437 | 9 897 |
| 4 | 1 | 87 965 | 58 % | 50 819 | 513 | 99.0 % | | | | | | 99.5 % | 513 | 35.8 | 4 184 | 8 152 |
| 5 | 1 | 26 280 | 76 % | 20 068 | 140 | 99.3 % | | | | | | 99.5 % | 77 | 17.3 | 2 027 | 26 020 |
| 6 | 2 | 151 475 | 28 % | 42 116 | 420 | 99.0 % | | | | | | 99.5 % | 414 | 65.5 | 7 548 | 18 203 |
| 7 | 3 | 237 250 | 70 % | 166 562 | 599 | 99.6 % | | | | | | | | | | |
| Amine-based (e.g. SCOT single train) | | | | | | | | | | | | | | | | |
| | Efficiency | ACC | Fixed OP | Variable OP | | | | | | | | | | | | |
| | 99.9 % | 7.4 % | 4 % TEC/yr | 5.1 €/tFF | | | | | | | | | | | | |
| Unit | S recovery efficiency | SO ₂ removed (From Base) | Total erected Cost (From Base) | Annualised Cost: Base to Sulfreeen | Cost-Effectiveness: Sulfreeen to SCOT | | | | | | | | | | | |
| | % | t/yr | M€ | k€/yr | €/t SO ₂ | | | | | | | | | | | |
| 1 | 99.9 % | 2 448 | 98.8 | 11 513 | 5 573 | | | | | | | | | | | |
| 2 | 99.9 % | 1 100 | 42.2 | 4 807 | 18 807 | | | | | | | | | | | |
| 3 | 99.9 % | 436 | 42.5 | 4 882 | 21 198 | | | | | | | | | | | |
| 4 | 99.9 % | 924 | 71.6 | 8 348 | 10 141 | | | | | | | | | | | |
| 5 | 99.9 % | 240 | 34.7 | 4 037 | 16 851 | | | | | | | | | | | |
| 6 | 99.9 % | 755 | 99.2 | 11 464 | 15 186 | | | | | | | | | | | |
| 7 | 99.9 % | 864 | 129.9 | 15 586 | 18 046 | | | | | | | | | | | |

Source: [139, CONCAWE 6/11 2011]

Driving force for implementation

To reduce sulphur emissions and recover sulphur.

Example plants

These techniques are widely used at refineries worldwide.

Table 4.95: Approximate number of commercial installations in the world

| Technique | Number of installations all over the world |
|--------------------------------|--|
| Beavon sulphur reduction (BSR) | >150 installations |
| Clauspol | >50 units |
| Sulfreen/hydrosulfreen | >150 units in operation |
| SuperClaus | >70 commercial plants |

Reference literature

[33, Lurgi 2005], [36, CONCAWE n°4/09 2009], [76, Hydrocarbon processing 2011], [107, Kohl 1997], [131, Ballaguet et al.2006], [139, CONCAWE 6/11 2011], [151, Sema, Sofres 1991], [160, Janson 1999], [163, FWE 1999], [165, Ademe 1999], [166, CONCAWE 1999], [177, WRA 1999], [183, HP 1998], [200, Gilbert 2000], [224, Kerkhof 2000], [244, France 2001], [Questionnaire n°11, 14, 18, 28 (spec. attachments)].

4.23.5.2.3 Wet gas scrubbing of the SRU off-gas

Techniques other than additional tail gas treatment of the SRU off-gas may be used, such as the SNO_x (a combined NO_x and SO_x abatement technique, see Section 4.23.8) or scrubber techniques, as presented in this section.

Description

As an alternative to an additional TGTU, some refineries have installed non-regenerative or regenerative scrubbers in order to abate sulphur emissions from their SRUs.

- Non-regenerative scrubbers used for this application can be of any type such as a jet ejector Venturi, high energy Venturi, magnesium-based or seawater scrubber. One type of scrubber that has been applied is a two-stage caustic scrubber (DynaWave) incorporating specific technologies for the enhancement of quenching and frothing effects in order to maximise the turbulent mixing and the gas absorption. These scrubbers are equipped with a droplet removal section and, optionally, Brinks mist eliminators.
- A regenerative scrubber based on the Cansolv technology, also used for the desulphurisation of waste gas in sulphuric acid plants and power plant boilers.

Achieved environmental benefits

The sulphur removal efficiency of the DynaWave non-regenerative scrubber is reported to be above 99.99 %. In related refineries, SRU sulphur recovery/removal efficiency reaches a 99.95 % rate.

Cross media effects

Water, reagent and energy consumption.

Economics and operational data

Not available.

Applicability

A DynaWave non-regenerative caustic scrubber has been in operation in two US refineries since 2004, and in another one since 2006.

A regenerative scrubber was installed for four months in 2006, and then it was shut down due to technical problems (independent from the Cansolv section).

Driving force for implementation

TGTU as described in Section 4.23.5.2.2 produces a concentrated H₂S stream which is recycled to the front end of SRUs for treatment. While this approach typically increases the sulphur recovery efficiency, it also tends to reduce the amount of fresh acid gas that can be potentially treated by the Claus process. Therefore, non-regenerative scrubbing is preferred for undersized or critical capacity SRUs, in order to avoid the SRU capacity decrease generated by the additional TGTU recovery capacity. With this approach, there is no concentrated H₂S stream recycled to the front end of the SRU.

Example plants

Sinclair Oil Corporation-Sinclair, Casper and Tula refineries (US).
BP-Cherry Point refinery (US).

4.23.5.2.4 Stored sulphur degassing

Description

In order to reduce the emissions of H₂S from the storage and transport of liquid sulphur, and to improve the product quality, the amount of H₂S and polysulphides in the sulphur can be reduced by oxidation or treatment with a suitable additive.

Achieved environmental benefits

Lowering H₂S concentrations in the gaseous phase of sulphur tanks reduces air releases during handling and improves operator safety. There are a number of techniques for sulphur degassing (SNEA or Aquisulf, Shell, Exxon and Texasgulf). With the Aquisulf degassing process, for example, residual H₂S in liquid sulphur can be reduced down to less than 10 mg/kg.

Cross-media effects

None in particular. Moreover, the reduction of H₂S in the liquid sulphur has a positive effect on the solidity of formed sulphur, and particularly on the sulphur slate strength.

Operational data

Not available.

Applicability

Fully applicable.

Driving force for implementation

To reduce operational hazards (toxicity and explosivity) and environmental nuisances due to H₂S desorbed and accumulated in the gaseous phase of fixed and transportation tanks.

Example plants

There were more than 50 Aquisulf sulphur degassing units, with capacities of 20 – 3 600 t/day, in operation at the end of 2005.

Reference literature

[33, Lurgi 2005], [207, TWG 2001].

4.23.5.3 Hydrogen sulphide and light mercaptan removal

Description

The system works with a fixed bed or batch-type granular reactant where iron compounds (Fe_3O_4 and Fe_2O_3) react with H_2S to form FeS_2 (pyrite).

Achieved environmental benefits

Processes for odour and low emission control features.

Applicability

Applications to waste water systems, land oil tanker vents, oil storage and transportation, and bitumen plants. Final polishing for odour control may be required to remove higher mercaptans and dimethyl disulphide.

Driving force for implementation

Processes for odour and emission control features.

Example plants

More than 1 000 applications worldwide. Processes are licensed under the SulfaTreat name.

Reference literature

[183, HP 1998]

4.23.5.4 Sulphur dioxide abatement techniques

In refinery flue-gases or waste gases, SO_2 may have unabated concentration levels of 1 500 – 7 500 mg/m^3 . Flue-gas desulphurisation (FGD) is a technique by which SO_2 is removed from these gases. FGD processes often involve an alkaline sorbent which captures SO_2 and transforms it into a solid product. Various FGD methods exist with varying SO_2 removal efficiencies. Recent years have shown the development of solvent/catalyst regenerative processes, in which the absorbing/concentrating medium is regenerated and reused. More information can be found in the CWW BREF [6, COM 2003].

Systems either of the regenerative type or the non-regenerative type exist for SO_x removal only, and also for the simultaneous removal of dust and NO_x . They are competitive with systems consisting of separate units for SO_2 elimination (i.e. wet scrubbers) and NO_x removal (i.e. SCR).

Description of the non-regenerative processes

Additive injection (AI) and *spray dry absorber (SD)* are scrubbing processes that remove SO_2 according to the same principle as the Wet Limestone Scrubber (WS). They involve a reaction with a Ca-based sorbent however, without the complicating requirements for producing a high-grade gypsum by-product (i.e. prescrubbing and oxidising). The by-product is a mixture of sulphites, sulphates and fly ash, for which there are few or no useful applications. The AI process provides moderate SO_2 removal at relatively low sulphur loads. A dry sorbent is injected into the furnace. The sorbent used is limestone or hydrated lime (for small boilers, more active sodium bicarbonate (NaHCO_3) is injected in the flue-gas duct).

Seawater scrubbing uses the natural alkaline constituents – bicarbonates – of seawater to remove SO_2 . This implies a potential for high removal efficiencies. The discharge will contain sulphate and chlorine ions, which are a natural constituent of seawater.

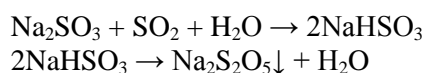
Walther (WA) is a process where SO_2 is absorbed by spray injection of aqueous ammonia, yielding ammonium sulphite. The sulphite is subsequently oxidised to sulphate. The ammonium salt solution from the scrubbing section is concentrated in an evaporation unit and granulated. The end product is a marketable fertiliser.

Wet limestone scrubber (WS) systems have been very much improved recently and have become less complex than the earlier systems. Generally a limestone/water slurry is used as the sorbent. Gypsum is produced by oxidation (aeration) in the sump of the absorber.

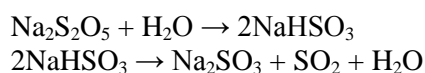
Description of the regenerative processes

Regenerative processes have been widely applied in refineries for SO₂ abatement. The first was the Wellman-Lord, then the Cansolv and the Labsorb process.

Wellman-Lord (WL) is the most widely used regenerative process. The process is based on sodium sulphite/bisulphite equilibrium. The first step is the absorption of SO₂ in a sodium sulphite aqueous solution, forming sodium bisulphite (NaHSO₃). By decreasing the temperature, sodium bisulphite is then converted into sodium pyrosulphite (Na₂S₂O₅) which precipitates, due to its much lower solubility:



By reheating this precipitate with water, the reversed reactions can occur, allowing the regeneration of SO₂, and the recycling of sodium sulphite into the process.



In US oil refineries where this process is operated for the treatment of SRU tail gases, the regenerated SO₂ is sent back to the sulphur recovery unit.

Cansolv is a regenerative technique which uses an aqueous amine solution to achieve selective absorption of sulphur dioxide. The gas to be treated is first saturated in a water prescrubber and is then contacted with the amine solution. The amine solution is regenerated by steam stripping. A slipstream of the amine needs to be purified to prevent the accumulation of salts. The scrubbing by-product is water-saturated SO₂ gas recovered by steam stripping.

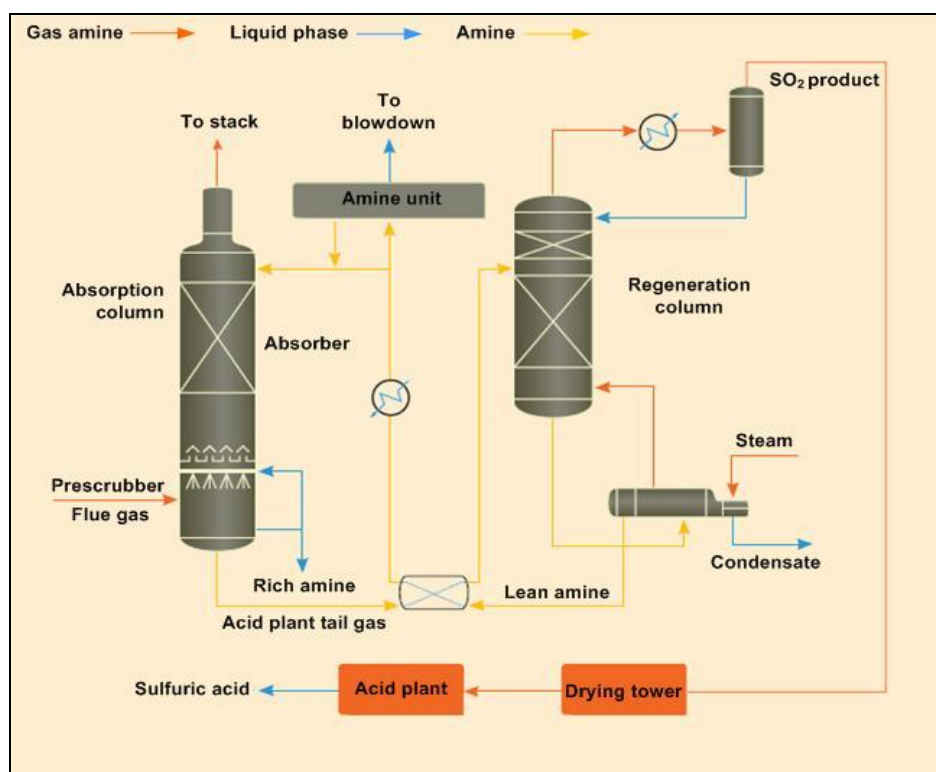


Figure 4.55: Process overview of the Cansolv regenerative scrubbing process

Labsorb is a regenerative scrubbing process which utilises an aqueous solution of sodium phosphate as a scrubbing buffer for the absorption of SO_2 . It generates a >90 % concentrated SO_2 stream that can be used as feed to a SRU or a sulphuric acid plant. The scrubbing solution is regenerated using low-pressure steam, which virtually eliminates the discharge of liquid effluents from the scrubber. Figure 4.56 below shows a simplified flow diagram of the Labsorb process, which consists of a first SO_2 absorption stage, followed by final regeneration stage.

At the absorption stage, the flue-gas is dedusted and quenched in a prescrubber fed with low-pH water recirculated from a make-up reservoir, before entering the absorbing tower itself. The absorbing agent used is a patented solution containing soda (NaOH) and phosphoric acid (H_2PO_4).

The regeneration involves a steam-heated evaporator for the release of the SO_2 absorbed in the rich solvent, followed by a gas/liquid separation, a stripper and a condenser. Concentrated SO_2 saturated in water leaves the condenser as recovered product, while water from the condenser returns to the process after steam stripping. A waste heat boiler before the unit can be used to produce low-pressure steam for buffer generation, further reducing the total operating costs.

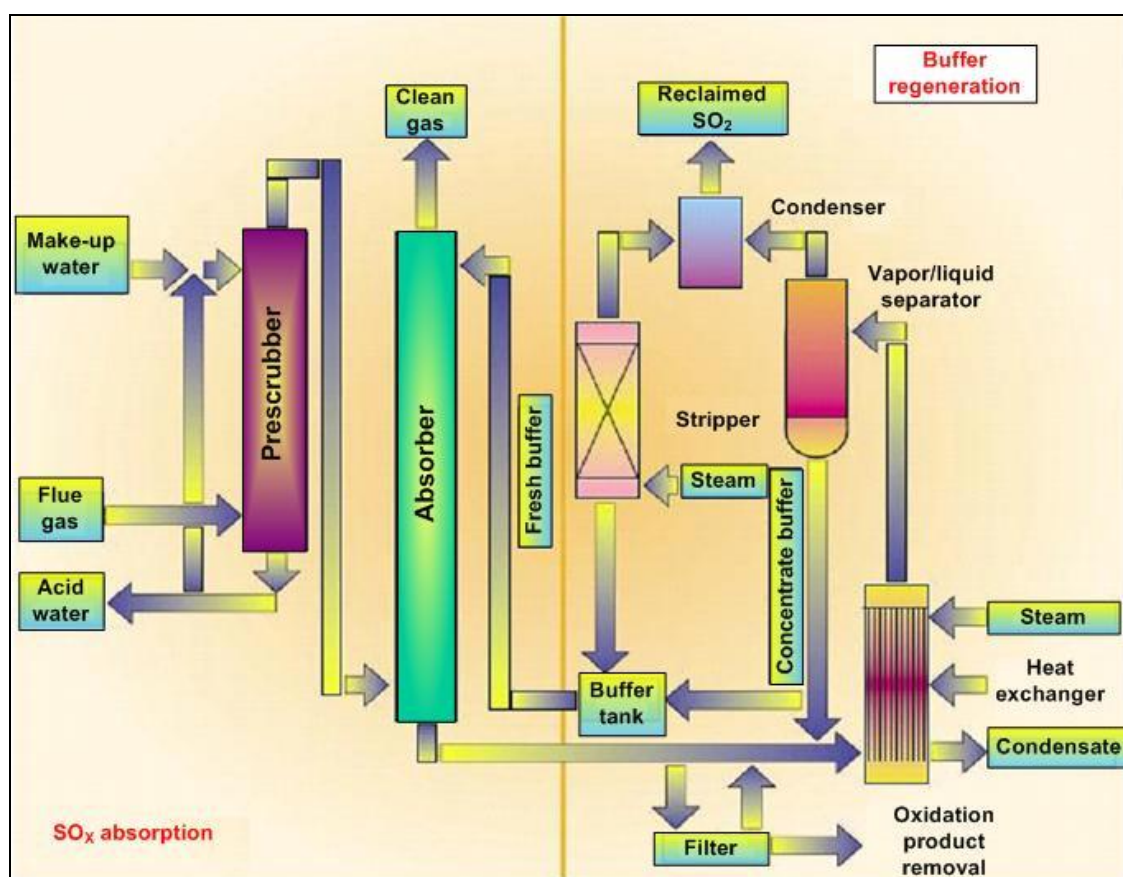


Figure 4.56: Simplified flow scheme of the Labsorb regenerative scrubbing process

SNO_x is a regenerative catalytic process which combines a pre-dedusting stage, followed by a WSA (described immediately below) and a SCR stage, whose purpose is to abate air pollutants in a combined technique. It reaches a high removal of SO_2 , NO_x and particulates. For more information see Section 4.23.8.

Waste gas sulphuric acid (WSA) is a solid-catalytic process allowing the condensation and the recuperation of concentrated sulphuric acid. It is well adapted to wet gases (no predrying stage required), but requires a careful pre-dedusting phase (maximum 1 mg/Nm^3) in order to maintain the specific potassium-vanadium catalyst performances. The gas temperature should be adjusted

to 400 – 420 °C. SO₂ reacts with residual O₂ and forms SO₃ which then combines with residual water vapour and is condensated at concentrations of 93 – 98 %. The adjustment of water and air concentrations is eventually required prior to the catalytic converter.

Achieved environmental benefits

A general overview is shown in the following summary table.

| Name of technique | Non-regenerative flue-gas desulphurisation | Regenerative catalytic flue-gas desulphurisation |
|---|--|--|
| Efficiency | 90 % (500 mg/Nm ³) | 95 – 98 % (250 – 100 mg/Nm ³) |
| Example: Capacity of the process: 5Mt/yr, 120 000 t/yr liquid refinery fuels, 180 000 t/yr refinery fuel gas. Volume of the flue-gas 1.68 x 10 ⁹ Nm ³ /yr. Pollutant: Initial concentration: 5 000 mg/Nm ³ (for liquid refinery fuels with 3 % S). Total quantity 8 400 t/yr. | | |

Detailed reported percentage reductions by technique are presented in Table 4.96.

Table 4.96: Achieved environmental benefits of various desulphurisation processes

| Desulphurisation technique | SO ₂ reduction (%) | Other benefits |
|--------------------------------|---------------------------------|---|
| Additive injection (AI) alone | 50 – 70 | |
| AI and spray dry absorber (SD) | >92 | Like with wet scrubbing, the SD system combines an effective removal of SO ₂ , SO ₃ , chlorine and fluorine (>90 % for sulphur compounds, 70 – 90 % for halides) |
| Seawater scrubbing | 85 – 98 | The acidic effluent from the absorber flows by gravity to a water treatment plant. Here, air is blown into the water to convert the absorbed SO ₂ into dissolved sulphate and to saturate the seawater with oxygen (COD treating). The pH is adjusted back to neutral partly by added seawater and partly by aeration. The effluent from the treatment plant is discharged directly back to the sea. |
| Walther | >88 | Product that can be sold as fertiliser. This product has to meet certain criteria (especially heavy metal content) |
| Wet Limestone Scrubber | 92 – 98 | If the chlorine content is low, this system produces a very low amount of waste water |
| Wellman-Lord | 98 (100 mg/Nm ³) | Sulphur can finally be recovered as a product. For the removal of SO ₃ , ammonia is injected, which leads to the formation of ammonium sulphate. Ammonium sulphate may be used as a fertiliser under certain circumstances (especially heavy metal content). |
| Cansolv | 98 | Sulphur by-products have a high purity and can be recovered for chemical |
| Labsorb | >85 | No external flue-gas cooling required upstream of the process. Very low chemical consumption. No residues produced other than limited amounts of sodium sulphate salts, which correspond to less than 1 % of waste mass generated by a wet limestone scrubber. The recovered SO ₂ has a high purity (>90 %) and can be recovered as a chemical or treated for sulphur recovery in existing SRUs. |
| SNO _x | 94 – 96.6 % | Up to 96 % for nitrogen oxides. Particulates are essentially completely removed. |
| WSA | 99 ⁽¹⁾ | NO _x is also reduced when used within the SNO _x process. In combination with a SCR, simultaneous reduction of 95 % NO _x can be achieved. |

Cross-media effects

Specific data on energy consumption for the various desulphurisation techniques (affecting CO₂ emissions) are not detailed. General information can be found in the LCP BREF [7, COM 2006].

Table 4.97: Cross-media effects of various desulphurisation processes

| Desulphurisation technique | Cross-media effects |
|---|---|
| Additive injection (AI) and Spray dry absorber (SD) | As the by-product generated by these techniques contains unreacted lime, it requires conditioning before disposal |
| AI process | The disposal of the by-product requires similar care to SD |
| Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption | These techniques generally produce a lot of waste |
| Seawater scrubbing | Some fly ash with associated heavy metals and organic substances is transferred to the seawater |
| Walther | The process does not generate solid by-products or liquid waste. If particulates with possible metals content are present in the flue-gas they appear together with the product. |
| Wet limestone scrubber | Waste water generated by the gypsum dewatering process contains suspended solids and trace elements (metals, chlorides) and is treated by sedimentation, flocculation and filter pressing. The filter cake is disposed of by landfill and the purified water is drained to the sewer. |
| Wellman-Lord | Dust: NH ₃ is injected to prevent the formation of SO ₃ . Therefore, up to 80 % of the ash consists of (NH ₄) ₂ SO ₄ , which can be used as a fertiliser or as a raw material for NH ₃ production. Waste water from the prescrubber has a sour water quality with a pH of around 2 and must be neutralised and stripped. The purified water may still contain up to 100 mg/l ammonia but, most often, values are in the range of 10 to 50 mg/l. |
| Cansolv | No detailed data |
| Labsorb | No significant side effect or disadvantage identified so far |
| SNO _x | See Section 4.23.8 |
| WSA | See Section 4.23.8 |

Operational data

Table 4.98: Operational data of various desulphurisation processes

| Desulphurisation technique | Operation data |
|---|---|
| Additive injection (AI) and Spray dry absorber (SD) | Being a dry process, corrosion conditions are less severe than is the case with WS. Hence, the scrubber is usually made of (uncoated) carbon steel. Calcium chlorides may yet prompt acid corrosion as they precipitate on the absorber walls and attract moisture. Recycling by-product with wet flue-gas to the sorbent make-up tank may suffer from plugging; regular cleaning is required. |
| AI process | The system is less effective as regards the removal of HCl, hence the fuel should not have a higher Cl content than approximately 0.3 % for corrosion prevention |
| Seawater scrubbing | The process offers simplicity, thus high availability |
| Walther | Chloride aerosols and a visible waste gas plume may occur when fuels with a high chlorine content are used. Aerosol formation can be mitigated by increased liquid to gas ratio in the absorber and the use of multiple tube filters. Deposits of sulphates can be removed by blowing with hot flue-gas or by water washing. NO _x has no influence on the FGD process as it does not react with ammonia. |
| Wet Limestone Scrubber | Through good engineering practice (liberal sizing of spray systems and mixers, applying washing on demisters, etc.), deposits and plugging of the various components can largely be avoided. For high-grade gypsum production, forced oxidation and good pH control is required. Furthermore, good quality limestone (>93 % purity in CaCO ₃) must be used and dust and trace elements, in particular chlorine, should be removed by prescrubbing of the raw gas and dewatering and optional washing of the product. Organic buffers (such as adipates and dibasic acid) can be used for pH control, thereby substantially enhancing the SO ₂ removal efficiency – typically by 4 %. Early corrosion problems have been overcome; often rubber lining is used in the absorber, requiring some care in view of abrasion damage. |
| Wellman-Lord | Operational aspects include problems with respect to fouling, corrosion and erosion. In the prescrubber, deposits of ammonium sulphate can occur. The evaporator is susceptible to wear by the abrasive salt slurry, corrosion during shutdowns and mechanical strains related to the high-speed centrifuge. |
| Cansolv | No detailed data |
| Labsorb | In the refining sector, this process has so far been applied only to FCC units |
| SNO _x | See Section 4.23.8 |
| WSA | No detailed data |

Applicability

As a general consideration, it is to be noted that the space requirement for scrubbers and ancillary equipment is an important factor for retrofit applications because of their size.

Table 4.99: Applicability of various desulphurisation processes

| Desulphurisation technique | Applicability |
|---|---|
| Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption | Typically used when the amounts of SO ₂ to recover are small because they produce waste, for example in small specialised refineries or small natural gas plants |
| Seawater scrubbing | Because particulates (including their heavy metals content) are transferred to the seawater, an efficient particulate abatement technique is necessary prior to the seawater scrubbing |
| Walther | Not suitable for fuels with an elevated sulphur content, as these result in increased ammonia slip due to the formation of ammonia sulphates. The sulphates are objectionable because of corrosion and aerosol emissions. |
| Wellman-Lord | Despite its excellent emission profile, the process complexity has discouraged widespread application |
| Cansolv | |
| Labsorb | In the refining sector, successfully applied to FCC units |
| SNO _x | This system is successfully used for on-site regeneration of H ₂ SO ₄ used in the alkylation unit, and for the treatment of H ₂ S gases (TGTUs) and off-gases from FCC unit regenerators and power plants fed with highly sulphurised fuels and residues |

Economics

Table 4.100: Economics of various desulphurisation processes

| Desulphurisation technique | Economics |
|---|--|
| AI process | 35 – 55 EUR/kWth (unit size: 75 – 300 MW). Annual operating cost roughly equals capital cost. |
| Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption | They are typically very cheap compared with other FGD techniques |
| Seawater scrubbing | Low capital costs and low operating costs (no bulk chemicals required, although sometimes magnesium hydroxide is used to enhance the alkalinity) |
| Wet limestone scrubber | 75 – 180 EUR/kWth (unit size: 75 – 300 MW). Annual operating cost roughly equals capital cost. Capital cost: EUR 10 – 20 million. Operating costs: EUR 1.6 – 4 million/yr. Flue-gas flows 200 000 – 650 000 Nm ³ /h. There are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, construction and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact. In some cases, these factors might be expected to increase the costs by some 50 %. |
| Wellman-Lord | The investment cost is estimated to be USD 50 million for a unit to handle a flue-gas flow rate of 500 000 Nm ³ /h and a SO ₂ concentration of 0.8 %. The cost includes licensing fees, engineering, equipment delivery, construction, commissioning and start-up services. |
| Cansolv | No information provided |
| Labsorb | This technique allows significant savings in operating costs compared to non-regenerative wet scrubbing processes, due to the very small consumption of chemicals used in the absorbing buffer make-up, and the intrinsic energy efficiency. See figures for FCC unit applications in Section 4.5.6. |
| SNO _x - WSA | See Section 4.23.8. |

Driving force for implementation

Table 4.101: Overview of the driving forces for the implementation of various desulphurisation processes

| Desulphurisation technique | Driving force for implementation |
|---|--|
| Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption | Abatement of small quantities of SO ₂ |
| Wellman-Lord | The process characteristics can suit the needs of particular industrial sites using high-sulphur fuels (in refineries in the US, Japan and Austria) |
| Cansolv | |
| Labsorb | Generates a by-product ready for conversion into liquid SO ₂ , sulphuric acid or elemental sulphur. Suits the need of industrial processes generating highly sulphurised flue-gases, as SRU tail gases and FCCs, but also fossil fuel-fired boilers and roaster gases from non-ferrous smelters |

Example plants

Table 4.102: Example plants where desulphurisation processes have been implemented

| Desulphurisation technique | Example plants |
|---|---|
| Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption | Applied in some small refineries and natural gas plants |
| Seawater scrubbing | The process has been applied to some extent (in 1994: 2 500 MW _e /47 units), also used for smelters, refineries and oil firing (at 3 % S) |
| Wet limestone scrubber | Operational experience with WS is highly satisfactory, demonstrated by high availability. This system is widely applied in power plants. In Germany, e.g. the TOTAL Mitteldeutschland refinery uses a wet lime desulphurisation process after the three oil-fired heaters of the power plant. The fuels used in this plant are vacuum residues, visbreaker residues and FCC slurry. |
| Wellman-Lord | More than 40 systems have been applied around the world, e.g. on FCCs |
| Cansolv | Cansolv units are used on sulphur plants, FCC and cokers |
| Labsorb | ESSO Norge in Slagentangen (Norway, 1994) - ENI S.p.A. in Sannazzaro (Italy, 2000) - VALERO refinery in Paulborough, NJ (US, 2002) |
| SNO _x - WSA | More than 25 units have been successfully installed worldwide. Applied in particular in AGIP refinery in Gela (Italy, 1997) and in OMV AG refinery in Schwechat (Austria, 2007) for power plants burning high-sulphur pet coke and residues. |

Reference literature

[21, ENI SpA 2009], [151, Sema, Sofres 1991], [108, Cansolv 2010], [163, FWE 1999], [183, HP 1998], [194, Winter 2000], [200, Gilbert 2000], [201, Manduzio 2000], [218, HMIP UK 2000], [221, Italy 2000].

4.23.5.5 Sulphur recovery units performances and variability

Table 4.103 shows the achieved sulphur recovery efficiency (% of S recovered) observed for a number of refinery sulphur recovery units (SRUs including TGTU) in Europe.

The sulphur recovery efficiency is calculated from the monitoring data available (emissions values expressed as SO₂ concentration after incineration from the time series) and based on several assumptions, such as:

- the SRU feed composition;
- the stack gas volume flow;
- the ratio acid gas/fuel gas for the incineration step (a value of 4 % is used for SRU 12).

Table 4.103: Sulphur recovery efficiency reported for a sample of European SRUs

| | Sulphur Recovery Unit (SRU) reference number | | | | | | | |
|--|--|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| | 1 | 2 | 4 | 6 | 8 | 9 | 11 | 12 |
| Claus process type | 2 Claus Stages | 2 Claus Stages | 2 Claus Stages | 2 Claus Stages | 2 Claus Stages | 2 Claus Stages | 2 Claus Stages | 3 Trains |
| Tail gas treatment unit (TGTU) type | SuperClaus | SuperClaus | ClausPol | SuperClaus | SuperClaus | SuperClaus | Hydro-Sulfreen | Amine-based |
| *SWS gas treated | YES | YES | YES | YES (**DSWS) | YES (**DSWS) | YES | YES | YES |
| Monthly min. % S recovery | 98.2 % | 98.0 % | 98.2 % | 99.2 % | 99.4 % | 98.8 % | 99.2 % | 99.91 – 99.93 % |
| Monthly max. % S recovery | 99.0 % | 98.7 % | 98.9 % | 99.6 % | 99.5 % | 99.3 % | 99.5 % | 99.98 – 99.97 % |
| *SWS: Sour Water Stripper **DSWS: Double Sour Water Stripper Source: [145, TWG CONCAWE 2012] | | | | | | | | |

In addition, an illustration of the variability of the sulphur recovery efficiency and the SO₂ concentration at the stack is shown in Figure 4.57 and Figure 4.58.

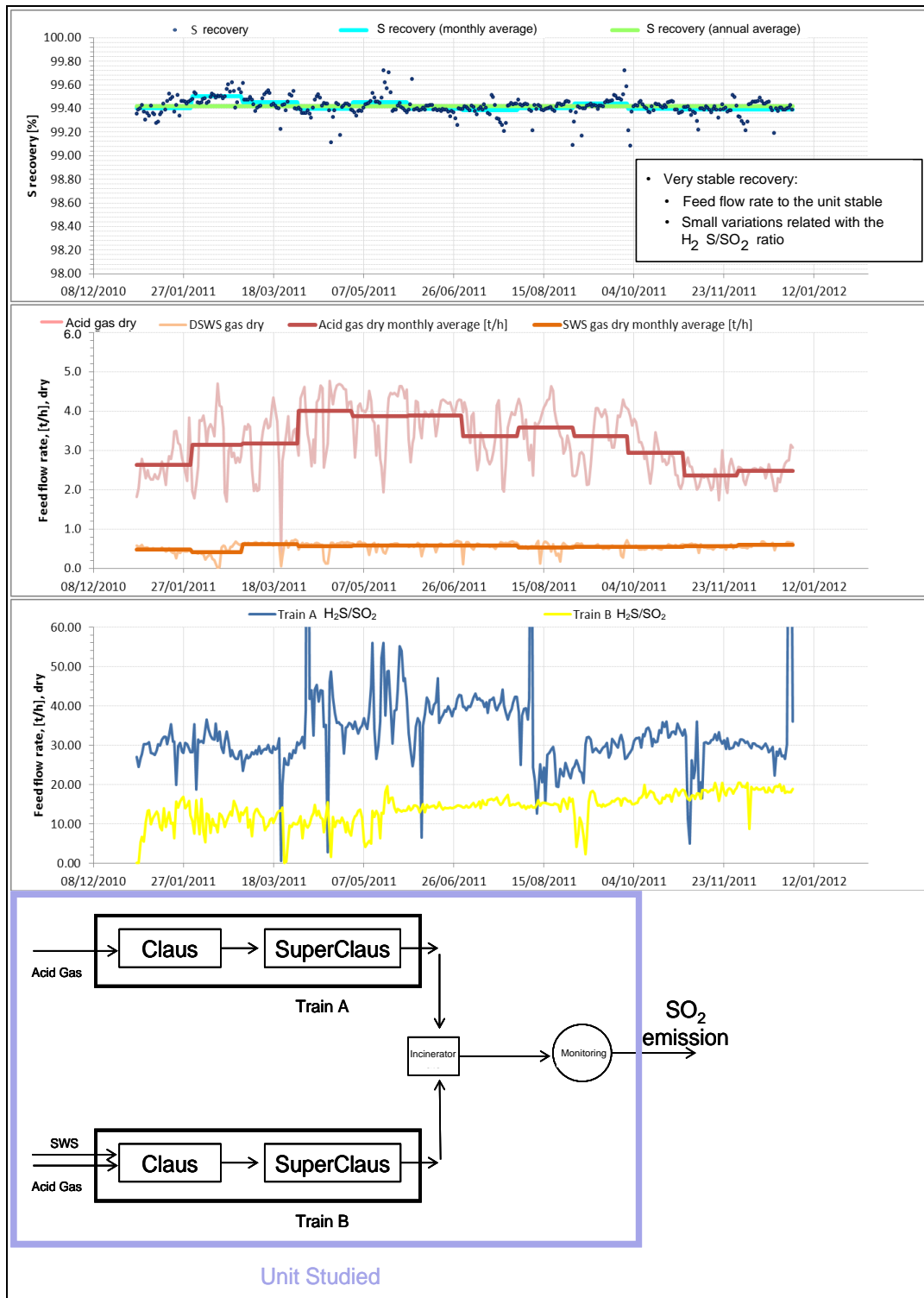


Figure 4.57: Variability of the daily sulphur recovery efficiency for a double train SRU equipped with a SuperClas tail gas treatment unit (data-set 8)

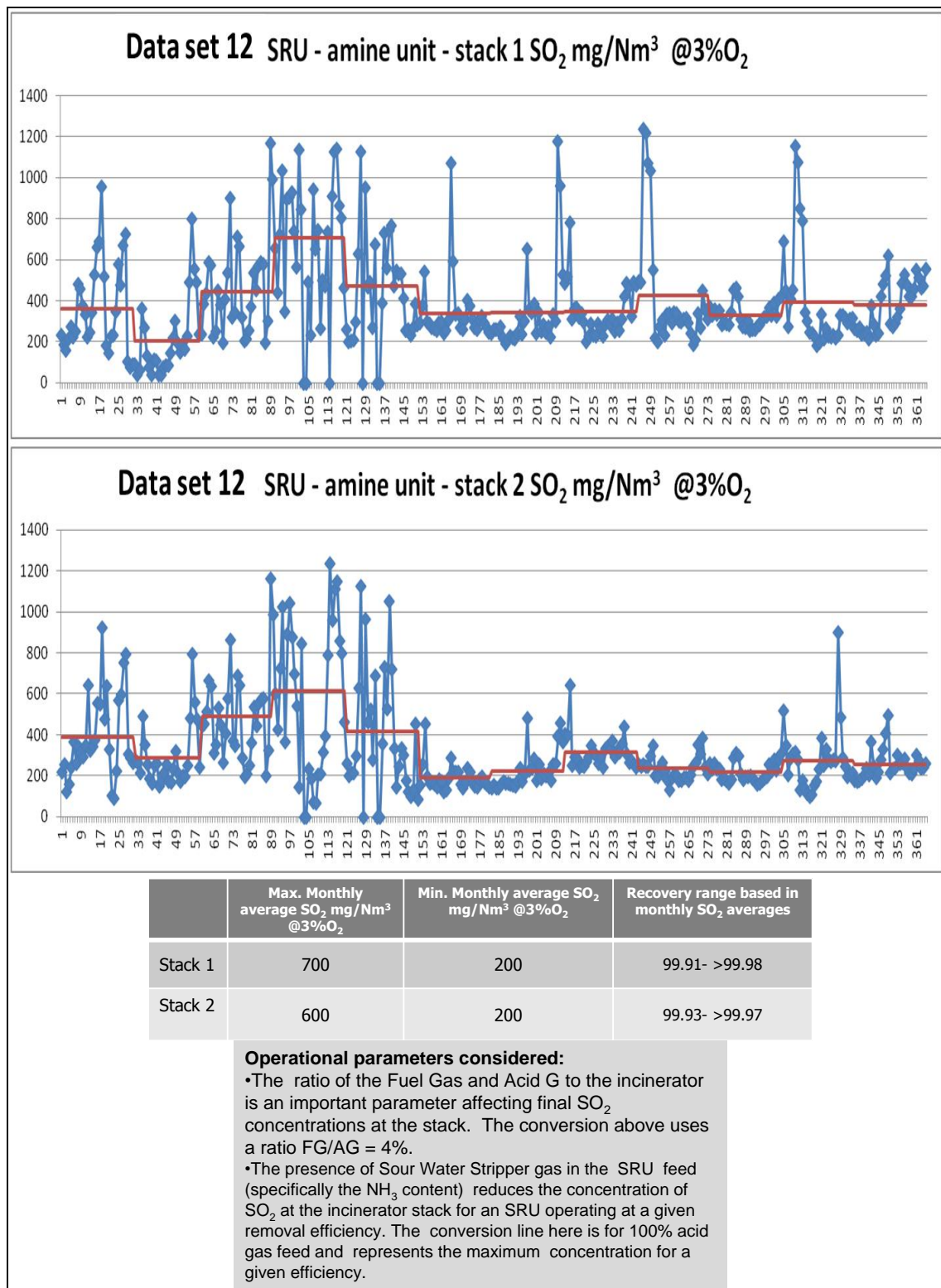


Figure 4.58: Variability of the daily sulphur recovery efficiency and SO₂ concentration at the stack for a three-train SRU equipped with two amine-based (SCOT) TGTUs (data-set 12)

4.23.6 VOC abatement techniques

When transferring liquids to vessels at atmospheric pressure, the existing mixture of vapour and gas (often air, but also inerts) in the receiving vessel is often emitted to the atmosphere. Such a loading operation is recognised as having an impact on the environment due to the presence of VOCs, a precursor of ozone. Directive 94/63/EC (EU Stage 1) requires that Member States prescribe the specific emission reduction measures as laid down in the annexes of the Directive. Also, the application of Vapour recovery units (VRUs) to prevent escape of these vapours to the atmosphere is specified in the Directive. VRUs aim for recovery of hydrocarbons for reuse. In some cases, recovery is not economic, and preference will be given to vapour destruction units (VDU). A more general term covering both options is vapour handling systems (VHS).

4.23.6.1 Techniques for the prevention, detection and control of fugitive VOC emissions

4.23.6.1.1 Techniques to prevent/reduce VOC emissions related to the process and plant design

Description

Techniques to reduce diffuse VOC emissions can be considered during both phases of the design:

- process design,
- plant design.

Process design

Process design conditions (e.g. temperature, pressure, vapour pressure of the process fluid) can influence the level of diffuse emissions. However, they are not chosen independently, they also depend on other parameters (e.g. catalyst activity, availability of utilities such as cooling air, water or steam) as well. In some operations with lower operating temperatures and pressures, where the fluid vapour pressures are lower, diffuse emissions are relatively lower [110, ESA 2005].

Techniques to reduce diffuse emissions resulting specifically from refinery process design can be:

- to achieve a balance between feed purity, processing steps, product quality and waste generation;
- to treat waste water streams which contain (mixtures of) VOCs by stripping, rectification and extraction or combinations of these techniques in order to remove the substances that could contribute to diffuse emissions (see waste water treatment, Section 4.24).

Plant design

The selection of plant components and the manner in which they are configured can both greatly influence the extent of diffuse emissions. For new units, there is a significant opportunity during the initial design phase to incorporate a wide range of techniques to reduce the potential for diffuse emissions. For existing plants, efforts can be made to incorporate many of these techniques over time as part of a process of continuous improvement.

Techniques to reduce diffuse emissions through the selection and configuration of refinery components include the following.

- Limiting the number of potential emission sources, such as by:
 - designing piping layout appropriately by:
 - minimising pipe run length;

- reducing the number of flanges (connectors) valves and screwed pipe fittings;
 - using welded fittings and pipes;
- reducing the number of pumps by using, if possible, other means of fluid transfer, e.g. by gravity.
- Maximising inherent process containment features, such as by:
 - enclosing (partially or completely) effluent drainage systems and tanks used for effluent storage/treatment;
 - minimising emissions during sampling by using closed sampling systems or in-line analysers;
 - installing a maintenance drain-out system to eliminate open discharges from drains.
- Selecting high-integrity equipment, such as:
 - valves with double packing seals or equally efficient equipment;
 - fitting high-integrity gaskets for critical applications;
 - pumps/compressors/agitators fitted with mechanical seals instead of packing;
 - magnetically driven pumps/compressors/agitators.
- Selecting appropriate materials for equipment, such as:
 - to ensure that all equipment (e.g. gaskets) is selected appropriately for each process application;
 - to avoid corrosion by appropriate selection of material of construction;
 - to prevent corrosion by lining or coating of equipment, painting pipes to prevent external corrosion and by using corrosion inhibitors of materials in contact with equipment;
 - to apply reactive paints, e.g. acid-sensitive paints applied on HF alkylation plant flanges.
- Facilitating monitoring and maintenance activities by ensuring good access to components that have the potential to leak.
- Collecting and treating emissions, such as conveying potentially collectable leaks (e.g. compressor seals, vents and purge lines) to flares or to flameless oxidisers.

Achieved environmental benefits

Prevention or reduction of diffuse VOC emissions.

Cross-media effects

The collection and containment of diffuse emissions can lead to explosive limits being reached as a consequence of the build-up of VOCs, e.g. where a cover is installed over a waste water treatment facility. This issue is subject to the Explosive Atmospheres Directives 99/92/EC (ATEX 137) and 94/9/EC (ATEX 100).

Environmental performance and operational data

Diffuse emissions can be estimated during process and plant design by using a technique that counts the number of potential emission point sources (flanges, valves, pumps, etc.) and applies standard emissions factors relating to the contained fluid. The reliability of an emission factor in a given application depends on the quality of the factor, the specific pollutants of interest, and the type of source.

Diffuse emissions from tanks can be estimated using the US EPA 'TANKS' software based on algorithms [113, US EPA 2006]. Methods to estimate diffuse emissions for other sources within refineries are provided in [111, CONCAWE 2009].

Technical considerations relevant to applicability

The aforementioned techniques to reduce diffuse emissions related to process and plant design are applicable to all new units that have potential diffuse emissions. For existing units, applicability may be limited by various constraints and efforts should be made to incorporate these techniques over time as part of the process of continuous improvement.

Economics

The cost of techniques to reduce diffuse emissions related to process and plant design depends on the specific installation. The costs are expected to be lower for new plants. In the long run, use of high-integrity equipment can reduce maintenance costs and the time dedicated to monitoring.

The reduction of diffuse emissions often provides opportunities for saving raw materials, recycling by-products, or avoiding the loss of final products, which all result in economic benefits.

Driving force for implementation

Reduction of VOC emissions.

The other driving forces for implementation include:

- reduction in material losses;
- safety of employees.

Example plants

All new chemical plants.

Reference literature

[6, COM 2003], [62, CONCAWE 2008], [109, IMPEL Network 2000], [110, ESA 2005], [111, CONCAWE 2009].

4.23.6.1.2 Techniques to prevent/reduce VOC emissions related to plant installation and commissioning

Description

The manner in which plant components are installed can greatly affect emissions, and this is an obvious issue prior to the first commissioning of a new plant or a new unit. However, the reinstallation of unit components as part of maintenance or project work on units already in operation can also have a significant impact on emissions.

Techniques to reduce diffuse VOC emissions related to the unit installation can include:

- to have in place strict and well-defined procedures for construction and assembly;
- to ensure that gaskets are installed correctly;
- to have robust commissioning and handover procedures in place to ensure that the unit is installed in line with the design requirements (e.g. the correct gaskets have been installed, the pipe runs do not include additional flanged connections).

Achieved environmental benefits

Prevention or reduction of diffuse emissions, particularly diffuse VOC emissions.

Cross-media effects

None.

Operational data

Diffuse VOC emissions from some preselected individual plant components or equipment types can be monitored as part of the plant commissioning and handover process in order to determine whether the plant has been installed correctly and in accordance with the design.

Applicability

These techniques are applicable to all new and existing units that have potential diffuse emissions.

Economics

The cost of techniques related to the unit installation to reduce diffuse emissions depends on the specific installation.

Reduction of diffuse emissions often provides opportunities for saving raw materials, recycling by-products, or avoiding the loss of final products, which all result in economic benefits.

Driving force for implementation

Reduction of VOC emissions, reduction in material losses and safety of employees.

Example plants

No information.

Reference literature

[109, IMPEL Network 2000], [110, ESA 2005].

4.23.6.1.3 Programme for the prevention, detection and control of VOC fugitive emissions

Description

Fugitive VOC emissions can be reduced by the detection and subsequent repair or replacement of leaking components. This is achieved by adopting a structured approach, commonly known as a leak detection and repair (LDAR) programme. A LDAR programme includes two fundamental steps:

- identification of the leaking components;
- repair of these leaks in order to minimise losses.

Leak detection

Two methods are currently available for the identification of leaks, and each method has its individual strengths and weaknesses. It is therefore necessary to decide upon the purpose behind a measurement exercise when selecting the method. In some circumstances, methods might need to be combined to fully understand the leak levels. Large-scale methods (see Section 3.26.1.3) may quickly locate the major emission areas, whereas maintenance may be improved using infrared cameras to locate the leakers.

Sniffing method (EN 15446)

Leak detection using hand-held analysers is called 'sniffing'. This method identifies leaking components by measuring the concentration of hydrocarbon vapours (in ppm) in the immediate vicinity of the leak with a flame ionisation detector (FID), a semi-conductive detector or a photo-ionisation detector (PID). The selection of the most suitable type of detector depends on the nature of the substance to be detected.

To check each potentially leaking component with hand-held analysers is time- and cost-intensive. Moreover, some leaking points might be difficult to access with the hand-held detectors to obtain a measurement. Sniffing surveys need careful preparation and are usually executed in campaigns that cover a specified portion of the refinery. Some companies have

therefore developed a ‘targeted monitoring’ approach in which additional emphasis is put on components with a higher frequency of leaks. For more details, see Section 3.26.1.3.

Optical gas imaging (OGI) method

The optical gas imaging method involves the detection of leaks with advanced hand-held infrared cameras that are specially developed for this purpose. Both active and passive systems exist: active systems use an adequately tuned laser beam, while passive systems detect infrared radiation reflected by the equipment. Gas imaging based on passive cameras was introduced in the early 2000s, and enables direct visualisation of both the leak and the leaking component and the recording of the images. In these recordings, gas clouds are visible as light or dark plumes.

Direct visualisation of leaks is of great value to improve the efficiency of maintenance on equipment as only the leaking equipment is repaired. Another advantage of the camera is the possibility to detect leaks under insulation and to screen from a distance, so that VOC emissions from components not accessible for sniffing can be located and repaired. However, as no reference protocol of use exists for these OGI instruments, detection limits and representativeness might differ from one user to the next (the type of gas and the minimum detected leak rate are generally provided on the supplier website). Furthermore, different commercially available instruments may lead to different sensitivities and detection efficiencies. Moreover, the intensity of the image projected by the camera depends on a number of factors and is not necessarily related to the concentration in the plume.

Infrared cameras therefore need to be employed with full knowledge of their limitations. These cameras can see only a small number of chemicals. For example, unless a BTEX leak is very large the camera will not detect it. In addition, they have relatively high detection limits (hundreds of ppm) and do not quantify or speciate the chemicals.

Some refineries are using infrared cameras before start-up to ensure the process is tight. Others are using cameras for safety purposes and for finding large leaks. For more details, see Section 3.26.1.3.

Leak repair

A staged approach is often applied to the repair of leaks, involving:

- An initial intervention such as tightening bolts to eliminate leaks from valve stems or flanges, installing tight caps on open ends. Such an intervention needs to be performed by skilled operators taking due recognition of necessary safety precautions.
- Repairing equipment with leaks that cannot be stopped by minor interventions. This may involve changing gaskets or packing, and may therefore require the equipment to be taken out of service.
- When no effective repair can be performed, considering the replacement of equipment.

The LDAR programmes based on sniffing typically do not include tanks and difficult-to-access plant areas. OGI and whole-plant measurements will identify problem areas that are not being monitored and allow them to be addressed. In many instances, they allow for more efficient allocation of maintenance efforts, by targeting the highest emitters first.

Achieved environmental benefits

Prevention and reduction of fugitive VOC emissions, which are one of the largest sources of refinery hydrocarbon emissions.

Environmental performance and operational data

One refinery in the US, which has been using the infrared camera for some years, has compared it with their existing LDAR approach using the sniffing method. They have found that the camera does not detect low level leaks and cannot be used as a substitute. However, they continue using it for safety and large leak detection purposes.

In Sweden, LDAR is done at all the refineries. Sniffing measurements are done twice a year at every potential leaking point that can be reached. If a unit is started up, additional sniffing measurements are carried out. Preem Refinery Lysekil does sniffing measurements on approximately 100 000 potential leaking points twice a year. Leak levels are defined as 100 ppm, 500 ppm and 900 ppm (as propane). For medium level leaks (500 ppm), action is taken as soon as possible to reduce the emission. At this refinery, since 1989, the number of leaks in the process area has decreased from 2 % to a level around 0.2 %. OGI is used to complement the sniffing method, although it has not been found that it can replace it. This is especially true for tank roofs which are difficult to monitor with sniffing; OGI has been found to give useful information on such emissions.

Cross-media effects

None.

Technical considerations relevant to applicability

Fully applicable. See descriptions and Section 3.26.1.3 for the applicability of each of the detection techniques.

Economics

In a typical US refinery with over 200 000 components, the annual cost for a LDAR programme is reported to exceed EUR 750 000 (actual cost USD 1 000 000, average 2010 USD/EUR exchange rate) with the US EPA Method 21 based on sniffing.

It is reported that full monitoring of a complex refinery can take six months or more to complete, and in one example costs were EUR 0.6 million (for 2006 in CONCAWE report 2008).

Driving force for implementation

Reduction of VOC emissions, reduction in material losses, and for the health and safety of employees.

Example plants

LDAR programmes have been used successfully worldwide to reduce VOC releases. See also Preem Refinery Lysekil (SE) under the Environmental performance and operational data paragraph in this section.

Reference literature

[6, COM 2003], [62, CONCAWE 2008], [110, ESA 2005], [111, CONCAWE 2009]
[113, US EPA 2006], [260, Energy Institute 2010].

4.23.6.2 Vapour recovery units (VRU)

Description

Vapour recovery units (VRUs) are installations designed for the reduction of volatile organic compound (VOC) emissions during loading and unloading operations. For a refinery, this is particularly relevant to gasoline and other volatile products, such as naphtha, and lighter products. Vapour recovery can also be used to abate emissions from fixed roof tanks storing volatile products which are not fitted with internal floating roofs (see Section 4.21.4). As VOC emission abatement by VRUs is only one aspect of total VOC control in a refinery, this section should be considered in combination with storage, handling and integrated refinery management. In addition to the VRU, a vapour collection system is required, as well as other equipment: vapour piping, detonation arresters, instrumentation, and possibly booster blowers, and vapour-holding tanks.

Detailed information, in particular for refinery product storage, is also provided in the EFS BREF [5, COM 2006]. Additional information is provided in the AEAT report

[115, Rudd et al.2001] on emissions during ship loading and in the ENTEC report on the implementation of Directive 94/63/EC for gasoline emission control [116, ENTEC 2009].

Vapour recovery systems involve two processes:

- separation of the hydrocarbons from air;
- liquefaction of the separated hydrocarbon vapours.

The separation processes that may be used to separate hydrocarbon vapours from the air are:

- pressure swing adsorption on activated carbon;
- absorption by washing in a low volatility absorbent fluid;
- selective membrane separation;
- condensation by cooling or compression (separation and liquefaction are combined in a single process).

The liquefaction processes applicable for separated hydrocarbon vapours are:

- absorption, normally into their own product;
- condensation;
- compression.

The following VRU systems are used for refined products:

- absorption in a cold lean oil stream;
- adsorption in twin bed pressure swing operation;
- indirect liquid condensation in a refrigerant heat exchanger;
- membrane separation by passage through a hydrocarbon selective surface.
- absorption: the vapour molecules dissolve in a suitable low volatility ('lean') absorbent (glycols or mineral oil fractions such as kerosene or reformat). The absorbent may need to be cooled to reduce its volatility (commonly at -25 °C to -30 °C for kerosene or reformat). It is then necessary to split the vapour from the absorbent by heating the absorbent/recovered product mix in a heat exchanger and then reabsorbing the rich product vapour in an appropriate stream, e.g. of the product being recovered or passing to a condenser, further processing unit or an incinerator. Absorption is not commonly used for gasoline vapour recovery in the EU because the technique is considered less efficient than, for example, adsorption.
- adsorption: the vapour molecules are retained by activate sites on the surface of adsorbent solid materials, like activated carbon (AC) or zeolite. The adsorbent needs periodical regeneration. Continuous processes have two vessels (beds) containing activated carbon, which cycle typically every 15 minutes between adsorption and regeneration modes. This regeneration of the carbon activity can be done using steam or, more commonly, vacuum pumps. The resulting desorbate is then absorbed (e.g. in a circulating gasoline component stream) in a downstream wash column (wash stage). The residual gas from the wash column (or separator) is sent to the inlet of the unit for re-adsorption. This technique is the one most commonly used for a gasoline VRU. See an example of a typical adsorption unit in Figure 4.59.

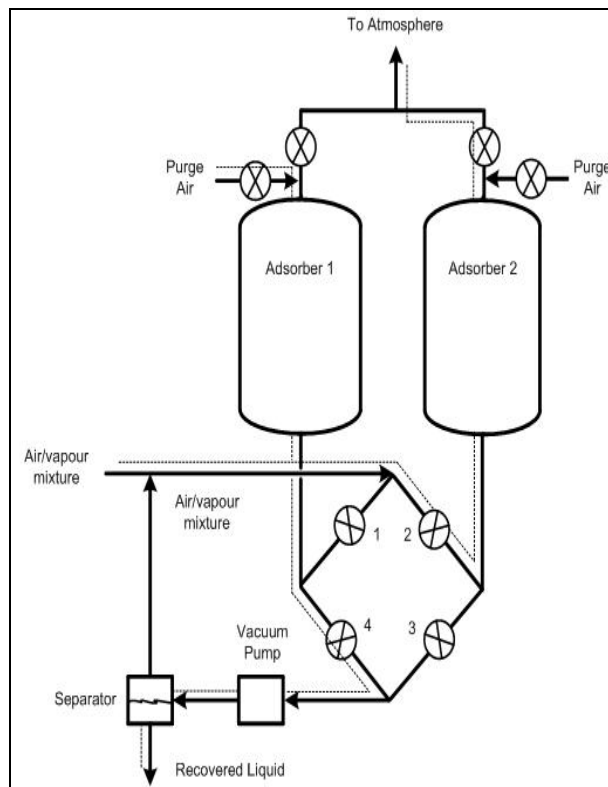


Figure 4.59: VRU activated carbon adsorption process

- membrane gas separation: the vapour molecules are processed through selective membranes to separate the vapour/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate). The efficiency of the separation process is dependent on the differential pressure across the membrane. For further purification, the membrane process can be combined with other processes. See an example of a typical membrane separation unit in Figure 4.60.

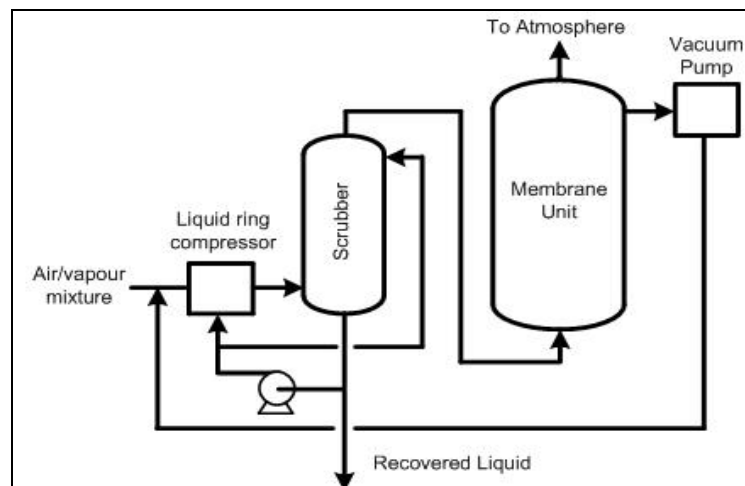


Figure 4.60: VRU membrane separation process

- refrigeration/condensation: by cooling the vapour/gas mixture, the vapour molecules condense on the surface of a cold heat exchanger and are separated as a liquid. A second stage (e.g. cryogenic condenser using liquid nitrogen) may be required to meet the emission limit. As the humidity leads to the icing-up of the heat exchanger, a two-stage

condensation process providing for alternate operation is required. This method can achieve low exit concentrations if the applied refrigeration temperature is low enough. The vapours are recovered as pure liquids (no waste), which can be returned directly to the storage tank.

- **hybrid systems:** combinations of techniques for the VRUs are commercially available to meet very low emissions standards. An example is a two-stage plant using membrane separation followed by adsorption.

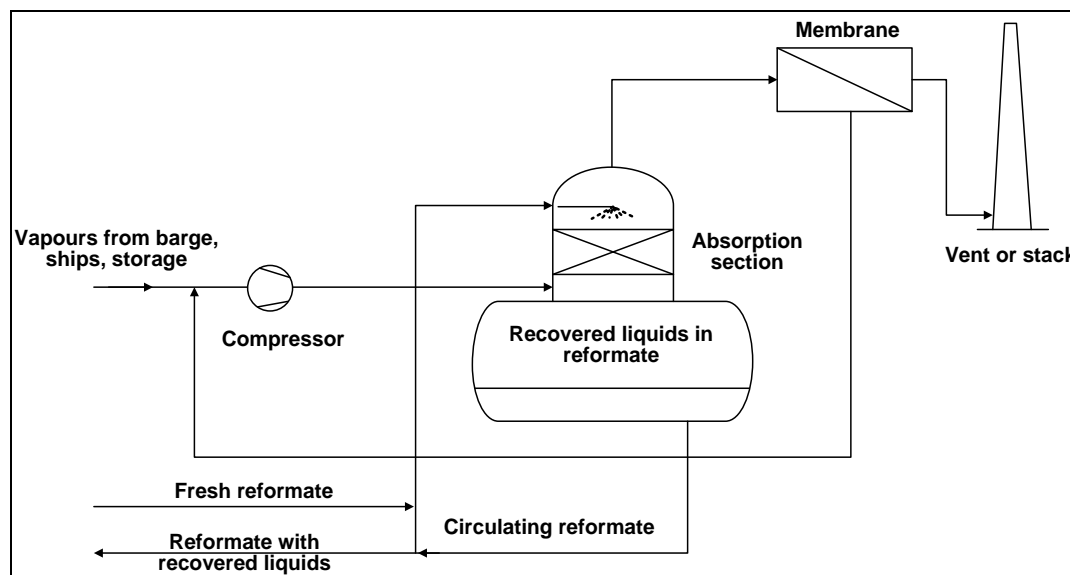


Figure 4.61: Simplified process flow scheme of a vapour recovery unit

Achieved environmental benefits

Emissions of the various systems are directly related to the abatement efficiency and can be as low as 10 mg/Nm^3 (without methane). With an abatement efficiency of 99.9 %, concentrations of 150 mg/Nm^3 (without methane) can be achieved for motor gasoline, as shown in Table 4.104. The emissions reduction achievable will depend upon the techniques used and the composition and concentration of the VOCs in the vapour stream being abated. For example, a gasoline vapour stream can have a NMVOC concentration of 1500 g/Nm^3 . Thus, to achieve a vent concentration of 150 mg/Nm^3 an abatement efficiency of 99.99 % is required.

A vapour recovery system for the loading of crude oil vessels can collect about 85 % of the total VOCs, which are condensed and reinjected into the crude feedstock.

Table 4.104 provides some data on the efficiency and environmental performance of vapour recovery units. Non-methane VOC (NMVOC) and benzene measurements can be performed through FID or GC.

Table 4.104: Emissions values for vapour recovery plants during the loading of motor gasolines

| Plant type | Recovery ⁽¹⁾ rates (%) | Average values attainable in continuous operation ⁽²⁾ ⁽³⁾ | |
|--|--------------------------------------|--|-------------------------------|
| | | NMVOC ⁽⁴⁾ (g/Nm ³) | Benzene (mg/Nm ³) |
| Single-stage condensation plant | 80 – 95 | 50 | 1 |
| Single-stage absorption plant | 90 – 97 | 35 | 50 |
| Single-stage adsorption and membrane separation plants | 90 – 99.5 | <10 ⁽⁵⁾ | 1 |
| Single-stage adsorption plants with supplementary blower | 99.98 | 0.15 | 1 |
| Compression, absorption and membrane separation ⁽⁶⁾ | 90 – 95 | NA | NA |
| Two-stage plants | 99.98 | 0.15 | 1 |

⁽¹⁾ As an indicator of performance level.
⁽²⁾ Expressed as an hourly average in continuous operation for consistency with 94/63/EC (Annex II).
⁽³⁾ These values are given for a HC concentration in the uncleaned gas of approx. 1 000 g/Nm³.
⁽⁴⁾ NMVOC: Non-methane volatile organic compounds. The methane contents in the vapours of the substances to be loaded can vary considerably. Absorption and adsorption processes cannot notably reduce methane emissions.
⁽⁵⁾ If single-stage plants are used as a preliminary stage for gas engines, a concentration of approx. 60 g/m³ is necessary for operation of the gas engine.
⁽⁶⁾ Compression followed by a two-stage recovery section: reabsorption of the VOCs into a fraction of the condensate being loaded followed by a membrane separation stage.
Source: Updated TWG 2010 ([36, CONCAWE 4/09 2009]), TWG- NO

Cross-media effects

The effects are related to energy consumption, especially for two-stage units, (for cooling, pumping, heating, vacuum); waste (adsorbent/membrane replacement); and water effluent (i.e. condensates from steam regeneration of adsorbent, defrost water from condensation units). Where explosive mixtures can occur, it is important that safeguards are implemented to limit the risk of ignition and ignition propagation.

Table 4.105: Cross-media effects associated with VRU techniques

| VRU technique | Cross-media effects |
|----------------------------|--|
| Adsorption | The adsorbent will require replacement - carbon life is generally greater than 10 years |
| Absorption | Waste water can be produced and requires appropriate treatment. Regeneration of the absorbent more than doubles the investment and energy costs. The only waste generated is the exhausted liquid which needs to be replaced once in many years. |
| Membrane separation | Requires a double set of vapour-moving equipment, i.e. a compressor and a vacuum pump. Potential for higher energy usage than for adsorption. |
| Condensation | Generates contaminated water effluent stream from defrost. Cooling systems have the potential for refrigerant losses and high energy usage. For cryogenic units, the production of liquid nitrogen is energy-intensive. |
| Hybrid (two-stage) systems | High energy consumers |

Environmental performance and operational data

In Gothenburg harbour (SE), three VRUs of the adsorption type (capacities of 1 500 m³/h, 2 000 m³/h and 2 400 m³/h respectively) serving four quays are implemented for the treatment of the vapours generated by the loading of around 1.4 million tonnes/year of gasoline. Calculated emissions have been reduced from 300 to 25 tonnes/yr, and the outlet concentration of total VOCs in the released stream is below 10 g/Nm³. The investment cost was around EUR 6.4 million (SEK 65 million) in 2001.

One of the biggest VRUs in the world ($36\,000\text{ Nm}^3/\text{h}$) has been in operation since 2008 in the Mongstad refinery (NO) for the treatment of vapours generated from the unloading of crude oil ships (two jetties). The installed power reaches 5.7 MW, and the recovery efficiency of the activated carbon bed filter system is estimated at around 85 % of total VOCs. The investment cost was around EUR 60 million (SEK 630 million) in 2008.

In Germany, recovery rates are reported that enable a minimum VOC emission reduction of 99 %.

In France, since the end of 1990, subsidies to support investment have been provided to companies (15 examples) to achieve more ambitious targets than the regulatory framework for recovery of vapours from loading facilities. One process uses adsorption on activated carbon with vacuum desorption. This process allows the VOC emission level to be reduced to $2\text{ g}/\text{Nm}^3$, below the regulatory target of $35\text{ g}/\text{Nm}^3$.

Figure 4.62 shows an example of the variability of emissions to air of NMVOC from a VRU (single-stage carbon adsorption unit) during the loading of a barge. The measurements are half-hourly averages from continuous monitoring during the loading (each operation taking place on a different day). The average over the entire period is $4.4\text{ g}/\text{Nm}^3$. The average over each loading operation is less than $10\text{ g}/\text{Nm}^3$. There are peaks over $10\text{ g}/\text{Nm}^3$ for 2 % of the time.

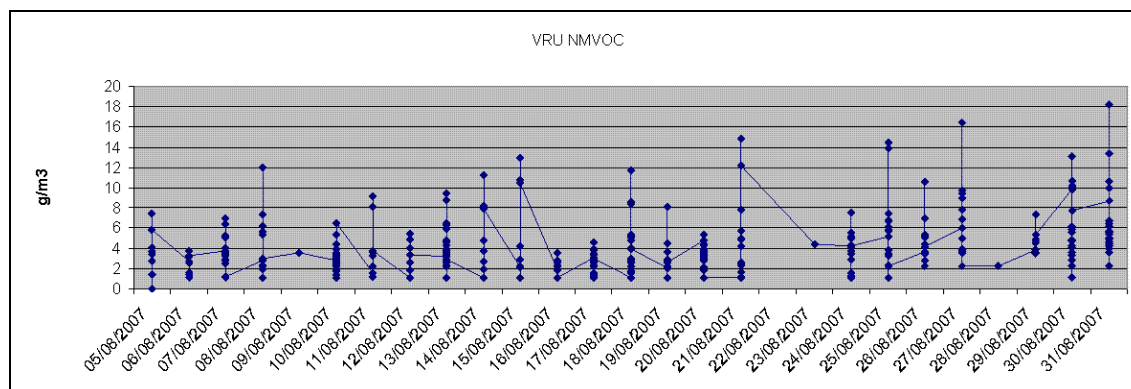


Figure 4.62: Variability of emissions to air from a VRU (data-set 12) over a month

Some of these peaks may be due to the start-up of the VRU, as seems to be the case for the two data-sets: number 8 (average over the seven-hour period: $0.2\text{ g}/\text{Nm}^3$) and number 9 (average: $6\text{ g}/\text{Nm}^3$), where variations over a day of both inlet and outlet concentrations from continuous monitoring are shown in Figure 4.63. The highest hourly values appear during the starting of the loading operation.

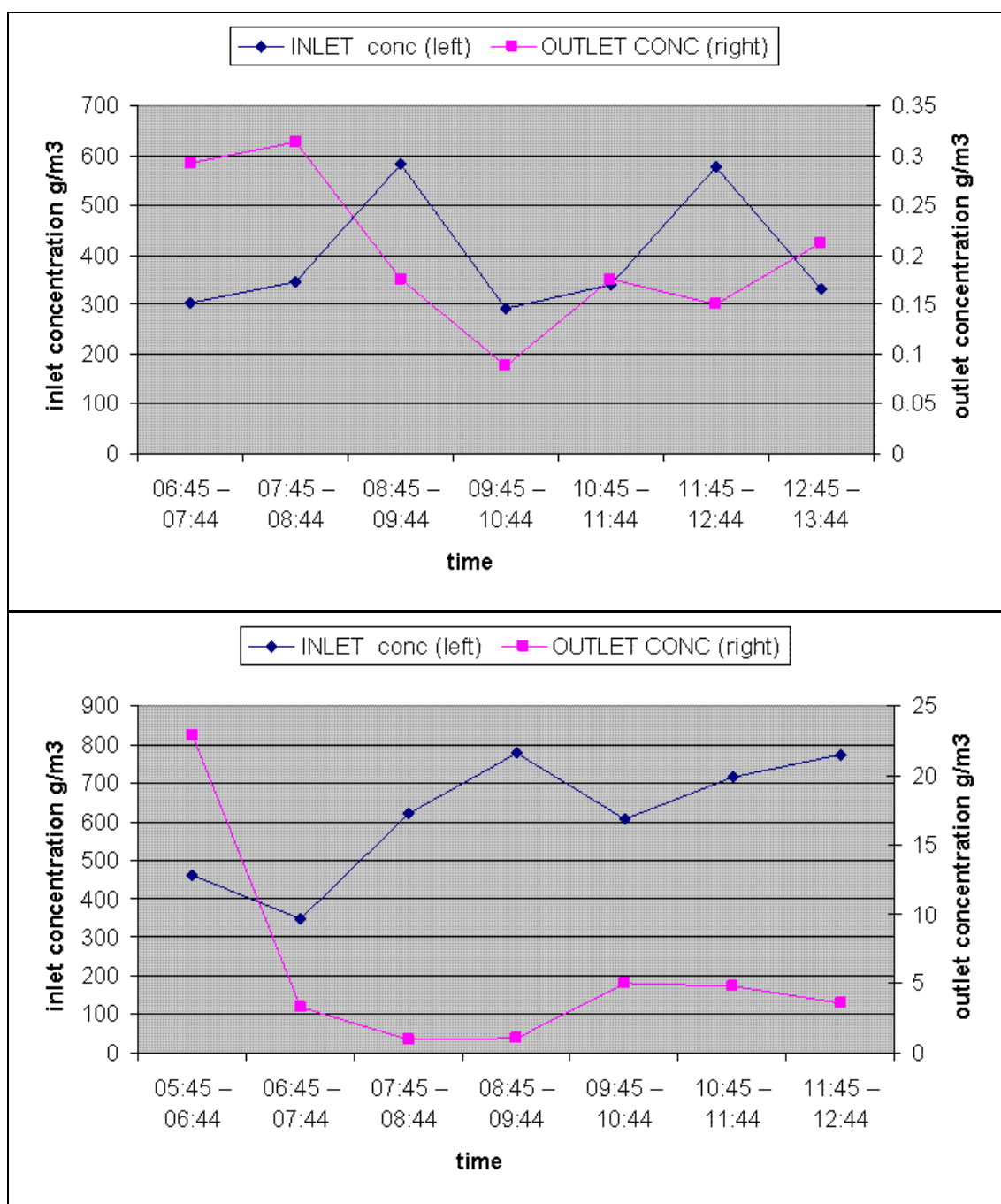


Figure 4.63: Variability of emissions to air from two VRUs (data-sets 8 and 9) over a day

Technical considerations relevant to applicability

Vapour recovery can be applied to crude loading (with the exception of adsorption unless a pretreatment such as sulphur stripper has been used, because of adsorbent fouling), dispatch product stations and in ship loading stations. However, for crude loading, it is less effective than systems for product loading, because the higher levels of methane and ethane in crude oil vapours are recovered with a low efficiency.

These systems are not applicable to unloading processes when the receiving tank is equipped with an external floating roof. Vapour recovery units are generally not considered applicable when the quantity of recovered product is small, e.g. for low volatility products.

VRUs occupy limited space. Usually they are preassembled and delivered skid-mounted. Commercial VRU capacities range from 500 Nm³/h to 2 000 Nm³/h. Adsorption systems are commonly used due to simplicity, good operability and high performance.

The main technical restrictions, including safety considerations, are described in Table 4.106. In addition, it is to be noted that one of the major constraints for VRUs is the potential incompatibility of the system with the vapours existing in the vessel due to the previous cargo when cleaning has not been properly done.

Table 4.106: Overview of the applicability of some VRU techniques

| VRU technique | Restriction in the applicability of the technique |
|---------------------|--|
| Adsorption | Handling of non-compatible compounds present in the vapour stream may either poison or destroy active carbon, e.g. H ₂ S in crude oil. Due to the heat of adsorption and the use of supplementary blowers, safety systems are required to ensure that auto-ignition does not occur. Appropriate monitoring to prevent it is also required. |
| Membrane separation | Well-suited to systems with large vapour volumes (compressor at the inlet to the membrane unit). For very small or variable vapour volumes, e.g. road tanker loading, common practice is to install a variable volume vapour-holding tank in the inlet vapour piping to the VRU. |
| Condensation | May require double heat exchanger set to enable unit defrosting during continuous operation. Light hydrocarbons form solid hydrates at low temperatures which can cause blockages. Flow variance has to be avoided to ensure efficient condensation. Very low-temperature equipment requires general safety measures. |
| Hybrid systems | Due to the complexity of operation, a high performance level is difficult to maintain |

Economics

Based on the AEAT report [115, Rudd et al.2001] on the abatement of ship loading emissions, Table 4.46 shows capital costs for a VRU plant for the various techniques over a range of vapour flows of up to 2 000 m³/h. These costs exclude civil engineering, provision of utility infrastructure and vapour collection systems. The additional corresponding costs are reported to be variable depending on the distance of the VRU to the loading facility (up to five times the cost of the VRU). The operating costs of the techniques consist of a component that is independent of throughput, which is in the range EUR 5 000 – 40 000/yr, plus a variable component which is approximately equal to EUR 0.05/t loaded.

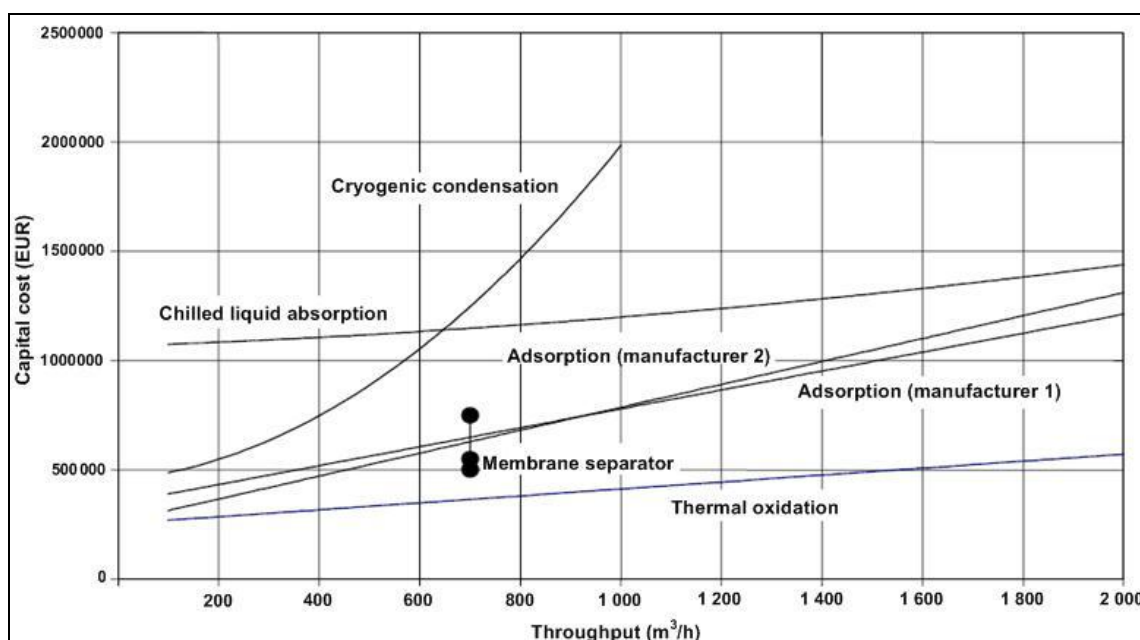


Figure 4.64: Capital costs for some VRU techniques and thermal oxidation (2001)

One report on the implementation of Directive 94/63/EC [116, ENTEC 2009] provides example cost data for a hypothetical single-stage adsorption-type unit operating at a recovery rate of 99.7 % and an inlet concentration of 1 160 g/Nm³, and therefore at an outlet concentration of 3.5 g/Nm³.

Table 4.107: Example cost data (2008) for a single-stage adsorption VRU operating at 3.5 g/Nm³

| Sites characteristics | VRU N°1 | VRU N°2 |
|---|---------|---------|
| Maximum loading rate (m ³ /h) | 273 | 1 090 |
| Capital cost excluding installation (EUR million) | 0.345 | 0.690 |
| Annual electricity usage costs (EUR) | 20 000 | 82 000 |

In France, the investment cost data (reported from the subsidy programme) given in Table 4.108 are available for the process operating at 2 g/Nm³.

Table 4.108: Examples of cost data for some French VRU sites

| Sites | Loading capacity (tonnes/year) | Instantaneous treatment flow (m ³ /h) | Year | Investment cost (EUR million) | Avoided tonnes of VOC/year |
|-------|--------------------------------|--|------|-------------------------------|----------------------------|
| No 1 | 1 200 000 | 3 000 | 2005 | 0.580 | 100 |
| No 2 | 192 500 | 800 | 1999 | 0.200 | 106 |
| No 3 | 1 000 000 | NA | 1998 | 0.980 | 130 |

VRUs with a capacity of 1 000 Nm³/h can involve a capital cost of EUR 2 million with an installation factor of 1.5 to 5, with marine loading applications being at the top end of the range.

The total capital investment strongly depends on site-specific factors, such as the number of loading vessels connected to the system, the distance between the berth and the emission control facility (cost of piping), the need for blowers and for safety systems (explosion and flame arresters). The capital costs can range from EUR 4 million to EUR 20 million for a VRU of

2 000 Nm³/h capacity. The investment costs can range from EUR 2 million to EUR 25 million for an efficiency of 99.2 %, implying an operating cost of EUR 0.02 – 1 million applied to loading operations (road, rail and internal refinery movements).

The investment costs corresponding to Gothenburg (SE) and Mongstad (NO) refineries (see previous paragraph on Environmental performance and operational data) were the following:

- at Gothenburg, three VRUs of the adsorption type (capacities of 1 500 m³/h, 2 000 m³/h and 2 400 m³/h respectively) serving four jetties cost around EUR 6.4 million (SEK 65 million) in 2001;
- at Mongstad, a 36 000 Nm³/h crude oil VRU cost around EUR 60 million (SEK 630 million) in 2008.

Quotation costs and power specifications for marine gasoline loading VRUs using different VRU technologies are the following, according to CONCAWE (2012).

Table 4.109: Examples of reported capital costs and power specifications for VRUs

| Technique | Capacity (m ³ /h) | Emission limit (g/Nm ³) | Cost (EUR million) | Power specifications (installed power) |
|---|------------------------------|-------------------------------------|---------------------------------------|--|
| Single-stage VRU/carbon adsorption | 2 500 | 10 | 1.05 | 425 kW |
| Single-stage VRU/membrane separation | 2 500 | 10 | 1.37 | 655 kW |
| Single-stage membrane separation | 3 500 | 10 | 2.7 | 785 kW |
| Two-stage membrane plus carbon adsorption | 3 500 | 0.15 | 3.5 | 980 kW |
| Single-stage carbon adsorption | 5 000 | 10 | Unit cost 3.5 Total system cost 23 | NA |

Source: [259, TWG CONCAWE 2012]

Driving force for implementation

Directive 94/63/EC on the control of VOC emissions resulting from the storage of petrol and its distribution prescribes the installation of vapour balancing lines and Vapour recovery units (VRUs) or vapour recovery systems (VRS) during gasoline loading/unloading activities in road and rail tankers and barges at refineries and terminals, to achieve an emission limit of 35 g/Nm³.

The Gothenburg Protocol specifies an emission limit of 10 g/Nm³ for total VOCs (in a 24-hour period) for gasoline VRUs, with an exclusion for the loading of seagoing ships. It requires the application of vapour recovery only for motor gasoline loading for road, rail tankers and barges and for throughputs of more than 5 000 m³/yr.

Example plants

Many VRUs at gasoline (un)loading installations for VOC emission reduction have been built in Europe following Stage 1 legislation or for crude unloading, e.g. at Gothenburg harbour (SE), Mongstad refinery (NO), in Germany and in France (see previous paragraphs on Environmental performance and operational data).

Reference literature

[5, COM 2006], [77, REF TWG 2010], [111, CONCAWE 2009], [115, Rudd et al.2001], [116, ENTEC 2009], [117, Germany - VDI 3479 2009], [151, Sema, Sofres 1991], [160, Janson 1999], [167, VDI 2000], [182, Ecker 1999], [183, HP 1998], [191, UBA Austria 1998], [201, Manduzio 2000], [207, TWG 2001], [228, TWG 2000], [259, TWG CONCAWE 2012].

4.23.6.3 Vapour destruction (VD)

Description

Apart from the conventional technique of VOC collection and destruction by routing to a flare system, two specific systems are relevant in this respect.

- Oxidation: the vapour molecules are converted to CO₂ and H₂O either by thermal oxidation at high temperatures or by catalytic oxidation at lower temperatures.
 - Thermal oxidation occurs typically in single chamber, refractory-lined oxidisers equipped with gas burner and a stack. If gasoline is present, the heat exchanger efficiency is limited and preheat temperatures are maintained below 180 °C to reduce the ignition risk. Operating temperatures range from 760 °C to 870 °C and residence times are typically one second or less.
 - Catalytic oxidation requires a catalyst to accelerate the rate of oxidation by adsorbing the oxygen and the VOCs on the surface. The catalyst enables the oxidation reaction to occur at lower temperatures than required by thermal oxidation: typically ranging from 320° to 540 °C. A first preheating step (electrically or with gas) takes place to reach a temperature necessary to initiate the VOCs' catalytic oxidation. An oxidation step occurs when the air is passed through a bed of solid catalysts.

Directive 94/63/EC (Stage 1) only allows oxidation in special situations, e.g. when vapour recovery is unsafe or technically impossible because of the volume of return vapour.

- Biofiltration: decomposition to CO₂ and H₂O is achieved at temperatures slightly above ambient by microorganisms located in a solid humidified support medium.

Achieved environmental benefits

Respective VOC elimination ratios achievable with such techniques are: thermal oxidation: 99 – 99.9 %, catalytic oxidation: 95 – 99 %, and biofilters: 95 – 99 %. However, the efficiency of the biofilters is controversial: since high removal efficiencies are only achieved with high inlet loads, emission concentrations well below 50 mg/Nm³ NMVOC are rarely achieved.

Biotreatment units need minimal maintenance and do not produce any noise. No fuel or chemicals are required. Biofilters remove or destroy aliphatic and aromatic hydrocarbons, other VOCs, H₂S and odours in the off-gases from process streams, tank vents, relief valves, soil vapour extraction and waste water treatments, etc.

Cross-media effects

Thermal oxidation can lead to unwanted combustion products such as NO_x, requiring extra treatment. Catalytic oxidation requires less energy to reach combustion temperatures, and can be competitive with thermal oxidation at low inlet concentrations. Thermal oxidation requires good primary and/or secondary safety measures to prevent explosions, while the efficiency of catalytic oxidation may be reduced by catalyst poisoning and ageing. The incineration of VOCs also generates CO₂. Additional fuel is consumed for the combustion of streams with low concentrations and for the preheating of catalysts.

Waste is only generated when biofilters are exhausted. No secondary pollutants or wastes are created.

Operational data

Usually, operating times are longer than two years. For biofilters, input air temperature should be 5 – 55 °C with an appropriate moisture level.

Applicability

Installation for the treatment of flows of 17 m³/h up to 135 000 m³/h are found in the literature.

For bioxidation, the method is highly suited for the treatment of continuous, constant composition air streams with low concentrations of organic pollutants. The method is not suitable for the direct treatment of the vapour/air mixtures often encountered in transshipments, because such mixtures have mostly higher vapour concentrations (>1 % v/v) and appear as sudden peak flows during the rather infrequent unloading operations. Biotreatment facilities are certainly sensitive to poisoning by unexpected compounds in the incoming vapour stream. Consequently, most of these systems need continuous monitoring to prevent the entrance of undesired compounds.

Biofiltration is only suitable for continuous, constant composition, low concentration vapour streams. These conditions are not typical of refining applications.

Economics

The economics of a thermal oxidation system with heat recovery will depend on many factors, including the calorific value of the waste stream. In 1998, a substantial payback was already expected based on the heat recovery from a thermal oxidiser furnished with a gas-to-gas heat exchanger that has an efficiency of 60 % and a gas flow of 4 720 l/s. Assuming natural gas was used as supplementary fuel, the costs reached around USD 20 per million of kcal and USD 0.08/kWh of electric power. For a system running 24 h/day, 350 d/yr, the payback time for the USD 0.2 million additional capital investment for a plant-type heat exchanger would be less than five months.

Biofiltration costs are significantly less than the other air pollution control techniques. Capital costs vary with flow rate and the destruction/removal efficiency. Capital costs start at about USD 15/m³/h. Operation and maintenance costs are extremely low because no fuel or chemicals are required.

Table 4.110: VOC thermal oxidation control technique applied to refinery

| Emission source | Refinery process units and equipment (installed and retrofitted) |
|---|---|
| Control technology | Collection of atmospheric VOCs and relief valves to flare/incineration system |
| Efficiency | Up to 99.5 % destruction efficiency in incineration |
| Investment costs | EUR 1.3 million for 5 Mt/yr refinery |
| Operating costs | EUR 3.0 million |
| Other impacts | Increase in CO ₂ emissions due to combustion |
| <i>Source: UN-ECE EC AIR/WG6/1998/5</i> | |

See also Figure 4.64 for the costs of thermal oxidation.

Driving force for implementation

Reduction of VOCs.

Example plants

Thermal oxidation: more than 107 units are operating worldwide.

Reference literature

[168, VROM 1999], [183, HP 1998].

4.23.7 Flares

Description

Flares are used for safety and the environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situations, upsets, unplanned events or unanticipated equipment failure. The flare is usually required to be smokeless. Flaring is both a source of air emissions and leads to the burning of potentially valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. For routine venting and planned shutdowns, flare gas recovery systems are to be used instead. More information is available in the CWW BREF [6, COM 2003].

Flare systems and designs

Flare systems can normally be divided into two main sections, i.e. the flare collection system with a flare knockout drum and the flare stack itself. When dealing with large refinery complexes, separate knockout drums may be installed in different process areas with 'blocking-in' facilities to allow maintenance during shutdowns of these areas.

Figure 4.65 shows a simplified process flow diagram of a flare system.

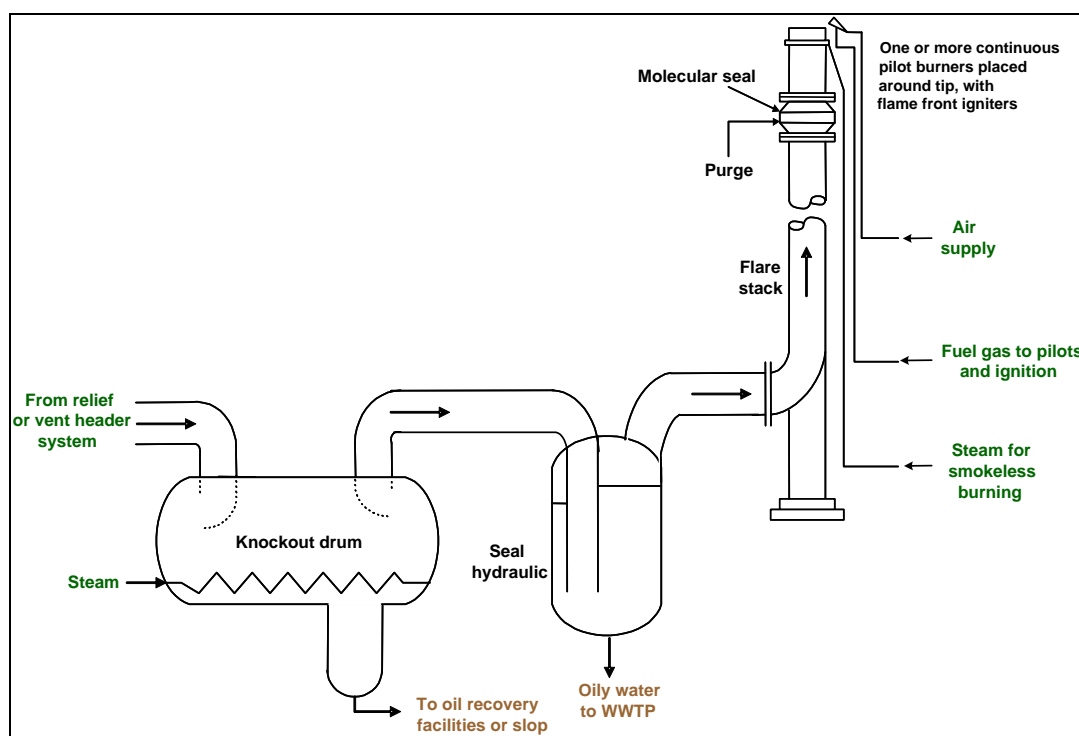


Figure 4.65: Simplified process flow diagram of a flare system

Many flare systems are available today for various purposes. The chosen flare system depends mainly on:

- the flow, pressure, temperature and composition of the gas that is flared;
- the requirements given for combustion efficiency, radiation, soot and noise;
- the availability and the access to steam, air and gas.

Flares can be categorised in several ways and the following distinctions can be made:

- the **type of flares**: elevated or placed on the ground (elevated are the most common flares and have the greatest capacity);

- the **flare system**: non-assisted flares (low or high pressure) or assisted flares (with steam, air, gas or water)
- the **zone in which the oxidation reaction occurs** and which includes the following categories: flame flares (open flame flares) or chamber flares (muffle and screen/shielded flares).

Compared to elevated flares, ground flares lead to poorer dispersion, because of the stack being nearer to the ground and therefore possibly resulting in environmental or health concerns (depending on the type of end products).

In chamber flares, combustion occurs inside a cylinder which enables them to operate without smoke formation, noise or radiation. A type of ground flare works as a **premixed surface combustion system** (an enclosed burner), where premixed gas and air burns on a permeable medium. (See [6, COM 2003]).

Table 4.111 shows an overview of the different main groups of flare systems. It also gives a brief description of each flare system, area of application and advantages and disadvantages regarding both environmental and operational consequences.

Extinguished flare systems also exist, where no permanent burning pilot flame is required, but a special mechanism is ignited when the speed of the gas exceeds a defined limit.

Non-assisted flare system

A flare that only burns natural gas without any supply of air or vapour is called a ***non-assisted flare***. It is used when non-smoking combustion can be achieved without external assistance. Depending on the pressure in the process equipment, it could lead to a low- or high-pressure flare. Pressurised gas provides a good mixing of air and waste gases and so reduces the exposure and smoke formation. On the other hand, it increases the noise level.

Assisted flare system

When the pressure in the waste gas to be flared is low, an external medium such as steam, air or gas can be used as the driving force. Depending on their respective availability, the following can be used:

- high-pressure steam for steam-assisted flare;
- high-pressure gas, for gas-assisted flare;
- air supply, for air-assisted flare;
- water being injected into the flare when low noise and radiation levels are required.

Table 4.111: Various flare system applications

| Flare systems | | Description | Application | Features |
|---------------------|-------------------------------------|--|---|--|
| Non-assisted flares | Low-pressure flare | Low-pressure flares are the simplest type of flare. Low-pressure flare tips are designed for a long service life. They are capable of flaring a wide range of waste streams and are primarily used for non-smoking gases. | Low-pressure flares can be used when non-smoking combustion can be achieved without external assistance. Low-pressure flares are used for maintenance and lower gas rates. | Cost-effective. Low maintenance costs. Stable, reliable combustion. |
| | High-pressure flare | High-pressure flares use the energy in the pressurised gas to create turbulent mixing and induce excess quantities of air for more complete combustion | High-pressure flares are used on land and offshore in order to achieve non-smoking combustion at large flaring rates. Can handle large quantities of flare gas at high pressure and has large capacity. | Cost-effective. Clean, efficient and smokeless combustion. Lower radiation. |
| Assisted flares | Steam-assisted flare | Steam-assisted flares are designed to dispose of heavier waste gases which have a greater tendency to smoke. Steam is injected into the waste stream as external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbons | Steam-assisted flares are employed in low-pressure applications to achieve smokeless flaring where high-pressure steam is available on site | Smokeless combustion. Low noise. Maximum energy efficiency. |
| | Air-assisted flare | Air supply is used as an external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbon waste gas. | Air-assisted flares can be employed for operations that require smokeless, low-pressure flares in areas where steam is not available as a smoke suppressant | Reduce smoke. Lower radiation. Lower noise generation. |
| | Gas-assisted flare | Gas injection is used as an external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbon waste gas. | Gas-assisted flares can be employed for operations that require smokeless, low-pressure flares in areas where high-pressure gas is available | Maximum combustion. Smokeless performance. |
| | High-pressure water injection flare | Water is injected into the flare to reduce radiation and flare noise. | For high-pressure applications that require low noise and radiation, and where water is available | Significantly reduces radiation and noise. Decreased operational and facility cost. |

Sources: [86, SFT 2009]

Techniques for flaring operations

Techniques to be applied to flares that may reduce emissions are given below.

- Use of pilot burners which give more reliable ignition to the vent gases because they are not affected by the wind.

- Steam injection in flaring stacks, which can reduce particulate matter emissions, when appropriately designed.
- Surplus refinery gas has to be flared, not vented. Knockout pots to remove liquids should be provided, with appropriate seals and liquid disposal systems to prevent the entrainment of liquids into the combustion zone. Water streams from seal drums should be routed to the sour water system.
- Flare gas recovery systems have been developed in which the flare gas is captured and compressed for other uses. Usually, recovered flare gas is treated and routed to the refinery fuel gas system. Depending upon the flare gas composition, recovered gas may have other uses. Reductions of flaring to ratios of 0.08 – 0.12 % of production in one natural gas plant in Norway have been reported.
- For minimisation of the soot formation in the flame, flow measurement with automatic steam control is applied in new installations; as well as luminosity measurements with automatic steam control, and remote visual observation using colour TV monitors in plant control rooms, allowing manual steam control and the detection of permanent availability of the pilot flame. The steam injection serves several purposes. Firstly, it improves the mixing of fuel and air by creating turbulence, and thus enhances combustion efficiency. Secondly, it protects the flare tip by keeping the flame away from the metal. Thirdly, the steam reduces soot emissions as it reacts with solid carbon particles to form CO, which is then further oxidised to CO₂. And lastly, the steam injection probably also reduces thermal NO_x formation. When hydrogen or very 'light' hydrocarbons are flared, steam injection is usually not applied as air-fuel mixing is often good and soot formation is unlikely.

Flare monitoring

Flare monitoring is needed in order to keep records of each event as part of the monitoring system of the refinery and to report to the local authority.

Flare systems should be equipped with adequate monitoring and control systems necessary to operate without smoke and evaluate emissions. Flares should be visually monitored under non-emergency conditions. Monitoring and control systems can be either automatic or manual (provided safety for the workers is ensured). They generally include a continuous flow measurement, remote visual observation using colour TV monitors, steam control and pilot flame detection.

Flare combustion efficiency can be monitored through the following operations:

- monitoring the mass flow rate and lower calorific value of the flare gas (e.g. by using automated gas sampling measurements);
- comparing the measured values to the design requirements to guarantee minimum combustion efficiency (e.g. 98 %).

Flare gas flow

Among the various non-intrusive measuring systems that are available and compatible with safety flaring applications, ultrasonic flow measuring has been the preferred choice in most new applications [29, Clearstone 2008]. Ultrasonic flow meters can be used on dry, but also on wet and dirty, gas streams, if the liquid content does not exceed ~0.5 % v/v. If greater amounts of liquids are anticipated, a liquids knockout system should be installed directly upstream of the flow meter. They are applicable to a wide volume range, offer high accuracy, do not require frequent calibration, and have no significant flow restriction. However, they need a sufficient length of straight pipe in order to ensure laminar flow measuring conditions, which can raise difficult constraints in the case of retrofitting. They also operate in temperature and pressure ranges which do not always correspond to actual process conditions. The approximate cost for such ultrasonic flow meters is estimated at EUR 0.5 million per measuring device [Questionnaire n°27].

Costs (2004) reported for an ultrasonic flow meter device are in the range of USD 20 000 – 30 000. Additional costs due to state-of-the-art site preparation, installation, calibration and connection may lead to an overall up-front cost of USD 100 000 (around EUR 79 400) per measuring device [258, Texas Commission on environmental quality 2010].

Like any monitoring device, the gas flow meters require the appropriate specifications (detection limit, measuring range) to deliver an accurate measurement. Alternative methods to estimate the flare gas flow based on operational parameters can be used, provided that a clear correlation is established.

Flare gas composition

Flare gas composition can be analysed by periodical sampling and subsequent laboratory analysis, or by continuous measurement devices. However, on-line gas chromatography for continuous measurement is highly sensitive to fouling and requires strict (and costly) pretreatment and conditioning of the samples, in order to remove water and particles before measurements.

As an example, the gas composition of two flares from a Norwegian refinery determined with online gas chromatography are provided in Table 4.112.

Table 4.112: Examples of flare gas composition

| Components | Main flare (mole %) | Sour gas flare (mole %) |
|--|---------------------|-------------------------|
| 1-Butene | 0.1 | 0.1 |
| C6+ | 0.7 | 1.5 |
| C-Butene | 0.1 | 0.1 |
| CO | 0.4 | 1 |
| CO ₂ | 0.5 | 0.4 |
| Ethane | 12.3 | 10 |
| Ethene (ethylene) | 2.8 | 5 |
| H ₂ | 38.9 | 35 |
| H ₂ S | 0.2 | 0.2 – 1 |
| 1-butane | 2.9 | 2 |
| I-butene | 0.1 | 0.1 |
| I-pentane | 0.9 | 0.4 |
| Methane | 18.4 | 23 |
| N ₂ | 5.6 | 16 |
| n-butane | 2.7 | 1 |
| n-pentane | 0.6 | 1 |
| O ₂ | 0.3 | 0.2 |
| Propane | 10.9 | 3 |
| Propene | 1.4 | 1 |
| t-butene | 0.1 | 0.1 |
| NB: The figures provided are based on normal conditions. H ₂ S concentration will vary with the amount of sour gas sent to the flare. Source: [86, SFT 2009] | | |

Flaring activity and emission records

On the above basis, flare gas emissions should be estimated and compiled in daily records of the site flaring activity. For each flaring episode, the record should document the measured or estimated flare gas composition, the measured or estimated flare gas quantity, and the episode duration.

The flare gas emissions can be calculated by using estimated or measured flows and concentrations (e.g. H₂S) that have been measured, together with emissions factors for NO_x and

CO. Available literature gives concentration values of around 100 – 400 mg/m³ for NO_x formed, and around 30 mg/m³ for CO released [28, Tebert et al. 2009].

For estimating VOC emissions, appropriate combustion efficiency shall be determined. In general, a minimum of 98 % may be assumed under optimised conditions and if guaranteed by the flare provider [6, COM 2003].

Table 4.113: Example of flare gas NO_x emissions factors used at a Norwegian refinery

| Component | Source | Emission factor | Basis for emission factor |
|-------------------------------|-------------------|-----------------|--|
| NO _x | Flare gas | 3.13 g/kg | Measurements in 2005 |
| | Flare (purge gas) | 3.13 g/kg | Measurements in 2005 |
| | Flare (sour gas) | 4.0 g/kg | Emission factor from NO _x tax |
| <i>Source:</i> [86, SFT 2009] | | | |

Achieved environmental benefits

Combustion efficiency, radiation, soot and noise depend on the flare system. Well-operated refinery flares typically achieve a conversion of 98 % to CO₂, 1.5 % are partially combusted products (almost all CO) and 0.5 % are unconverted. Enclosed ground flares have reduced noise and smoke compared to elevated flares. However, the initial cost often makes them undesirable for large releases when compared to elevated systems.

Environmental performance and operational data

In order to achieve a combustion that is as complete as possible, the flare should be operated with a minimum flame temperature of 800 – 850 °C. Flare efficiency is generally maximised through assessment of the heating value of the flared streams and by minimising flame quenching, for example by over steaming. Since air present in the stack can create a potentially explosive mixture with the incoming flare gas during low flare gas loads, a continuous stream of purge gas is required. When using nitrogen, a smaller purging rate is required. Very often, a molecular water seal is employed, which allows for using a lower purging rate.

Table 4.114: Example of two flares' design conditions in a UK refinery (2007)

| Emission Source | Units | 1st flare | 2nd flare |
|---|----------|---------------|--------------|
| Height | m | 91 | 137 |
| Type of system | | High pressure | Low pressure |
| Maximum capacity | tonnes/h | 397 | 680 |
| Smokeless capacity | tonnes/h | 34 | 68 |
| Pilot gas consumption | kg/h | 1.9 | 1.9 |
| Purge gas consumption | kg/h | 22.7 | 12.5 |
| Steam consumption ⁽¹⁾ | tonnes/h | 11.8 | 21.8 |
| SO ₂ emission ⁽²⁾ | kg/h | 0.074 | 0.043 |
| ⁽¹⁾ Steam consumption at maximum smokeless capacity. | | | |
| ⁽²⁾ From pilot gas and purge gas. | | | |

Cross-media effects

Flare emissions will include, in addition to NO_x, CO from combustion, and a part of uncombusted flared gas compounds (e.g. VOCs, H₂S, SO₂), thus causing potential health concerns and odour nuisances (mainly for ground flares).

Flare seal water typically needs treatment before release. Steam injection for combustion enhancement and soot blowing spends thermal energy. The use of ground flares can lead to the potential accumulation of a vapour cloud in the event of a flare malfunction; special safety dispersion systems are therefore usually included in the ground flare system. As a consequence, instrumentation for monitoring and controlling ground flares is typically more stringent than for

an elevated system. In addition, flares, especially steam-assisted ones, generate noise and light nuisances.

Technical considerations relevant to applicability

The flaring of toxic gases (never via a ground flare) requires special considerations. To ensure safe operation during periods when the flare may not have a flame present, ground-level concentration calculations for hazardous components should be performed assuming the flare is used as a vent only. Other safeguards may be necessary to mitigate ground-level exposure hazards. Reliable continuous pilot monitoring is considered critical when flaring toxic gases.

Due to different burning characteristics of the gases, a separate sour gas flare is usually provided; this flare could be equipped with different burners than the hydrocarbon flare, to allow for more efficient combustion of sour gases (H₂S).

Economics

No detailed data received.

Driving force for implementation

Some local regulations (e.g. South Coast Air Quality Management District (SCAQMD), California, US) require flare minimisation plans. The seven refineries (30 flares) in the SCAQMD area are now required to have continuous flow gas monitors, continuous gas heating value monitors, and semi-continuous total sulphur concentration monitors.

The main other driving force for implementation is health and safety.

Example plants

Flares are common in refineries. Two examples of low flaring ratio refineries in Sweden are provided in Section 3.23.3.

Reference literature

[6, COM 2003], [86, SFT 2009], [118, VITO 2009], [148, Irish EPA 1993], [159, WB 1998], [167, VDI 2000], [168, VROM 1999], [258, Texas Commission on environmental quality 2010], [Questionnaire number 43, 27].

4.23.8 The SNO_x combined technique to abate air pollutants

Description

The SNO_x plant is designed to remove SO₂, NO_x and particulate matter from combustion flue-gases. It is based on a first dust removal stage (by an ESP), followed by catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NO_x is reduced to N₂.

The only additional material necessary is the ammonia used for the NO_x removal. Furthermore, natural gas and water are needed, besides small quantities of silicone oil for the acid mist control unit.

The process produces 94 – 95 % pure sulphuric acid (H₂SO₄) for sale. The system employs a catalytic converter to oxidise SO₂ to SO₃ at a temperature of 400 – 420 °C. This temperature level allows a DeNO_x, operating at 380 °C, to be well fitted in the process. High NO_x removal at high NH₃ slip is possible with no risk of precipitation of ammonium sulphates, as the reactor temperatures are above the decomposition temperature (350 °C) and any NH₃ slip is destroyed in the SO₂/SO₃ oxidiser.

The process produces no waste water or waste products, nor does it consume any chemical apart from ammonia for NO_x control. The high removal of dust is required by the H₂SO₄ production

step. Dedusting with an efficiency consistently at 99.9 % is required so as to avoid frequent clean-up of the SO₂/SO₃ converter and to maintain good product quality.

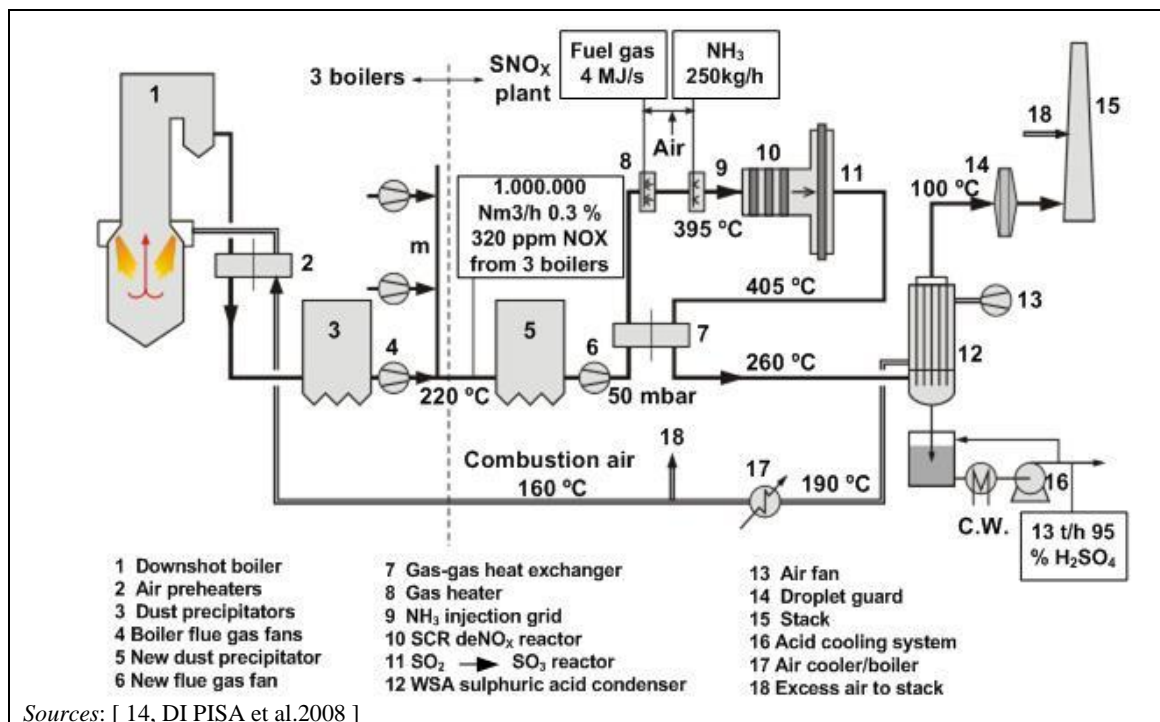


Figure 4.66: SNO_x process scheme in the Gela refinery

As shown in Figure 4.66, the heat from the acid condenser (operating between 240 – 100 °C, hydrating SO₃ and condensing the resulting acid product) is used as the first step in preheating combustion air. The recovered heat, produced by the conversion process, is substantial and makes up for the power demand when the sulphur content in the fuel (oil or coal) is 2 – 3 %. Areas relating to dust that require attention in operation are the HTEP, the SO₂/SO₃ converter and the acid falling-film condenser (made of borosilicate glass tubes). Formation of acid mist (aerosol) in the condenser is avoided by a patented heterogeneous nucleation control, which is essential for the operation of WSA and SNO_x plants.

Achieved environmental benefits

They are summarised as follows:

- removal of 94 – 98 % of SO₂ and SO₃, 90 – 96 % of NO_x, and essentially all PM;
- process able to treat high SO₂ concentration flue-gas;
- high removal of SO₂, together with NO_x and particulates removal (see Table 4.115);
- low additional environmental impacts: no raw material required (only ammonia consumption for NO_x control), no waste water or waste production;
- no cooling water consumption;
- production, as a by-product of the process, of H₂SO₄ at a commercial grade suitable for sale;
- high heat recovery.

Cross-media effects

The electrical consumption corresponds to an installed power of around 10 MW_e for a 1 million Nm³/h unit.

Operational data

In Gela, the SNO_x unit treats the flue-gas from three pet coke firing boilers (producing 3 x 380 t/h of HP steam) and is designed for 1 million Nm³/h, with an upstream SO₂ concentration ranging from 6 900 mg/Nm³ to 13 200 mg/Nm³ (at 6.7 % v/v humidity and 5 % O₂ content) due to the particular refining process based on high-sulphur crude. The ammonia injection rate used to operate the SCR section is about 200 kg/h. The H₂SO₄ production (95 % H₂SO₄ concentration) reaches 13 t/h with a 5.5 % sulphur pet coke.

Table 4.115: SNO_x performance from a 72-hour test run after 5 months of operation (Gela)

| Parameters | Units | Results |
|--|--------------------|---------|
| Flue-gas flow rate (wet) ⁽¹⁾ | Nm ³ /h | 971 000 |
| Inlet NO _x (as NO ₂) | mg/Nm ³ | 451 |
| Outlet NO _x (as NO ₂) | mg/Nm ³ | 42 |
| NO _x reduction efficiency ⁽²⁾ | % | 90.5 |
| Inlet SO ₂ | mg/Nm ³ | 8 243 |
| Outlet SO ₂ | mg/Nm ³ | 288 |
| SO ₂ reduction efficiency | % | 96.5 |
| Outlet SO ₃ ⁽³⁾ | ppm | 3 |
| Outlet NH ₃ | ppm | NA |
| H ₂ SO ₄ concentration | % w/w | 95 |
| Electricity consumption (Blowers, ESP, pumps) | MWh | 132 377 |
| Ammonia consumption | kg/h | 238 |
| Methane consumption | Nm ³ /h | 456 |
| NB: NA: not available | | |
| ⁽¹⁾ Maximum flue-gases available from the boilers during the test run. | | |
| ⁽²⁾ After NH ₃ grid distribution adjustment, efficiency raised to 93 – 95 %. | | |
| ⁽³⁾ More accurate measurement shows 2 ppm. | | |
| Source: [14, DI PISA et al. 2008] | | |

Table 4.117 provides results from a 72-hour test run which was performed in order to check the maximum efficiency after complete renewal of catalyst beds. Additional information based on the Gela site monitoring under average operating conditions from 2003 show the following abatement efficiency in Table 4.117 [257, TWG IT 2012].

Table 4.116 SNO_x performance under average operating conditions (Gela)

| Parameters | Units | Results |
|--|--------------------|------------|
| Flue-gas flow rate to SNO _x | Nm ³ /h | 1 000 000 |
| SO₂ overall abatement efficiency | % | 94 |
| SO ₂ concentration, in flue-gas to SNO _x ⁽¹⁾ | mg/Nm ³ | 9 994 |
| SO ₂ concentration in flue-gas to stack ⁽¹⁾ | mg/Nm ³ | 600 |
| SO ₂ concentration in flue-gas to stack, dry and at 5.4% O ₂ | mg/Nm ³ | 627 |
| NO_x overall abatement efficiency | % | 90 |
| NO _x concentration in flue-gas to SNO _x ⁽¹⁾ ⁽²⁾ | mg/Nm ³ | 636 |
| NO _x concentration in flue-gas to stack ⁽¹⁾ ⁽²⁾ | mg/Nm ³ | 64 |
| NO _x in flue-gas to stack, dry and at 5.4 % O ₂ ⁽²⁾ | mg/Nm ³ | 68 |
| NB: | | |
| ⁽¹⁾ These values refer to a humidity content of 6.7 % v/v and an oxygen content of 5 %. | | |
| ⁽²⁾ NO _x expressed as NO ₂ . | | |
| Source: [257, TWG IT 2012] | | |

In Schwechat, the SNO_x unit treats the flue-gas from a central CHP plant fuelled with heavy residues from the thermal cracker, together with the tail gases received from the SRU.

Table 4.117: SNO_x performance (OMV Schwechat)

| Parameters | Units | Results |
|---|------------------------------|------------|
| Flue-gas flow rate (wet) | Nm ³ /h | 820 000 |
| Inlet NO _x (as NO ₂) | mg/Nm ³ | Max. 700 |
| Design outlet NO _x (as NO ₂) | mg/Nm ³ | <200 |
| NO _x reduction efficiency | % | >87 % |
| Inlet SO ₂ | mg/Nm ³ | Max. 8 000 |
| Design outlet SO ₂ | mg/Nm ³ | <200 |
| SO ₂ reduction efficiency | % | >96.6 % |
| Outlet SO ₃ | ppm | NA |
| Outlet NH ₃ | ppm | <1 |
| H ₂ SO ₄ concentration | % w/w | NA |
| Electricity consumption (Blowers, ESP, pumps) | MW _e installed | NA |
| Ammonia consumption | kg/h | NA |
| Methane consumption | Nm ³ /h | NA |
| NB: NA: not available | | |
| Source: [54, Gallauner et al.2009] | | |

Applicability

The Gela refinery SNO_x plant was reported in May 2008 to have been operated with 96 % availability on average (including annual planned stops), and no decrease in performance from its start-up in September 1999 (according to measured conversion rates and pressure drops). After a 72 500-hour run, the plant had its first general shutdown (1 056 hours) for maintenance in June 2006. Only 50 % (12 beds out of 24) of the desulphurisation catalyst were replaced. The SCR catalyst is still the same as at the beginning of the plant commissioning.

The Schwechat refinery SNO_x plant started operation in October 2007 and is designed for a turnaround period of a minimum of six years.

Economics

A SNO_x plant designed for a flue-gas load of 1.0 million Nm³/h had a cost of EUR 100 million. For such a unit, reported annual maintenance costs are EUR 4.176 million for a five-year period between 2003 and 2007, as shown in Table 4.118.

Table 4.118: Maintenance costs (in thousand EUR) of the Gela SNO_x plant for 2003 – 2007

| Year | 2003 | 2004 | 2005 | 2006 | 2007 | TOTAL |
|------------------------------------|--------|--------|--------|----------|--------|----------|
| Routine expenses | 211.08 | 423.71 | 130.04 | 177.70 | 124.79 | 1 067.32 |
| Extraordinary | 112.33 | 123.21 | 11.96 | 128.84 | 129.79 | 506.13 |
| Ordinary outage | 14.22 | 83.03 | 348.11 | 1 882.41 | 274.79 | 2 602.56 |
| TOTAL | 337.63 | 629.95 | 490.11 | 2 188.95 | 529.37 | 4 176.01 |
| Source: [14, DI PISA et al.2008] | | | | | | |

Driving force for implementation

Reducing air emissions (SO_x, NO_x and dust) from burning high-sulphur fuels (e.g. pet coke), together with recovering a sulphuric acid by-product at commercial specifications.

Example plants

AGIP Refinery in Gela, Italy (1999), OMV Refinery in Schwechat, Austria (2007), NEFO Power Plant in Nordjyllandsvaerket, Denmark (2005). According to TOPSOE Company, six more units were contracted in 2008 for a total of over 5 million Nm³/h of flue-gas.

Reference literature

[13, TOPSOE 2006], [14, DI PISA et al.2008], [15, 2008 Refining Process Handbook], [221, Italy 2000], [257, TWG IT 2012].

4.23.9 Odour pollution prevention and control techniques**Use of nitrates for odour control****Description**

This technique can be used to reduce the odour generated by any equipment (e.g. storage tanks, sewage systems, oil/water separators) where anoxic conditions can lead to the formation of hydrogen sulphide and other odorous mercaptans in contaminated waters from the biodegradation of sulphur organic compounds by bacteria. This technique consists of adding nitrate-based products in septic water areas, in order to replace bacteria feedstock and to favour the development of denitrifying bacteria, which will both reduce added nitrates in nitrogen and existing hydrogen sulphide in sulphates. Nitrate solution can also be injected in bioreactors

Achieved environmental benefits

In favourable conditions of use, hydrogen sulphide and mercaptans can be significantly reduced and even virtually eliminated. For example:

- The addition of a 400 mg/l nitrate solution in a septic ballast water tank with an appropriate decreasing dosing rate can eliminate a pre-existing concentration of 115 mg/l of hydrogen sulphide by >90 % after the first 24 hours. After 36 hours, hydrogen sulphide can be almost eliminated, while the nitrate concentration in the treated water remains below 20 mg/l.
- A 250 m³ biofilm reactor was installed in 1995 for the treatment of ballast waters which have to be stored for long periods (weeks) before being discharged to the waste water treatment plant of a refinery in Norway. The reactor treats up to 600 m³/h of water and removes up to 60 kg H₂S per hour.

The reduction of hydrogen sulphide and mercaptans concentration in the septic pieces of equipment concerned also has major beneficial effects on occupational safety for the operators intervening on such equipment.

Cross-media effects

Inappropriate dosing can lead to an excessive contamination of nitrates in the treated waters.

Operational data

The available literature reports the following.

- A consumption of around 90 – 150 t/yr of nitrate-based solution needed for treating the water bottom of a large crude oil tank, avoiding odorous (and dangerous) releases of hydrogen sulphide during draining operations.
- A consumption of 100 t/yr for the treatment of a ballast water tank kept at a high level as it doubles as a reserved water source for firefighting. Nitrate-based solution is injected when pumping additional water into the tank, and further additions are made shortly before any discharges.

Applicability

This technique is fully applicable.

Economics

In 2009, the price of the chemical additives used for implementing this technique was around EUR 350 – 550/tonne, depending on the chemicals price fluctuations, related logistics and number of injection sites at the refinery. In some cases, there could be additional costs for a storage tank and for pumping system rent.

Driving force for implementation

Elimination of hazardous situations and reduction of odours generated by septic waters.

Example plants

This technique is reported to be currently implemented in various refineries operated in the UK and Norway.

Reference literature

[55, Dixon et al.2009]

4.24 Waste water treatments

This section is complementary to the previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for waste waters generated by oil and gas refining.

For a given technique, available data on the way it can be applied and the results it allows on particular processes or units have been given in the related sections. The information provided here aims at completing this information on broader aspects, in particular environmental benefits, cross-media effects, operational data, and applicability issues which will not be repeated in other sections.

The purpose of the waste water treatment plant is to control the amount of substances in waste water that are emitted to the receiving water body. The configurations of waste water treatment plants may differ from one refinery site to another due to site-specific needs and requirements. The techniques applied at a site may include:

- measures directed at managing waste streams at or near their source;
- measures applied downstream of sources to segregate and manage waste streams together that have similar and/or compatible and/or synergistic properties;
- end-of-pipe techniques.

When the techniques applied include a biological treatment step, a pretreatment system of sufficient configuration, capacity, and coupled with best practices is necessary to assure there is no inhibition of the efficiency of the biological step.

Techniques to consider in the determination of BAT include, but are not be limited to:

- techniques that are applied to control routine and non-routine operation and/or maintenance for waste water sources that are characterised to have variable flow and/or substance loads, including:
 - tank water draws;
 - vacuum truck movements;
 - equipment clearing activities for maintenance;
- waste water source control and efficient operation of the waste water treatment systems;
- practices that include utilisation of special procedures and/or temporary equipment to ensure performances are respected when necessary to manage special circumstances such as:
 - spills;
 - loss of containment;
 - misdirected flows;
 - high flow rates;
 - high substance load rates from malfunctions;
 - incidents;
 - routine and/or major maintenance activities.
- practices that assure the cause of deviations in expected treatment performances are identified, and that immediate corrective action is taken to minimise the impact on performance, and corrective actions are implemented to minimise the risk of a repeat occurrence of the deviation.

If needed, further and more in-depth information about these techniques, and others can also be found in the CWW BREF [6, COM 2003].

As illustrated in Figure 4.67, a distinction can be made within the global waste water treatment between:

- the collection of waste water from units after possible pretreatment;
- the removal of insoluble substances: first step recovering oil;
- the removal of insoluble substances: second step recovering suspended solids and dispersed oil;
- the removal of soluble substances, including biological treatment (with possible nitrification/denitrification) and clarification;
- additional treatment systems.

Techniques to consider for these treatment steps are described respectively in Sections 4.24.4.1, 4.24.4.2, 4.24.4.3 and 4.24.5.

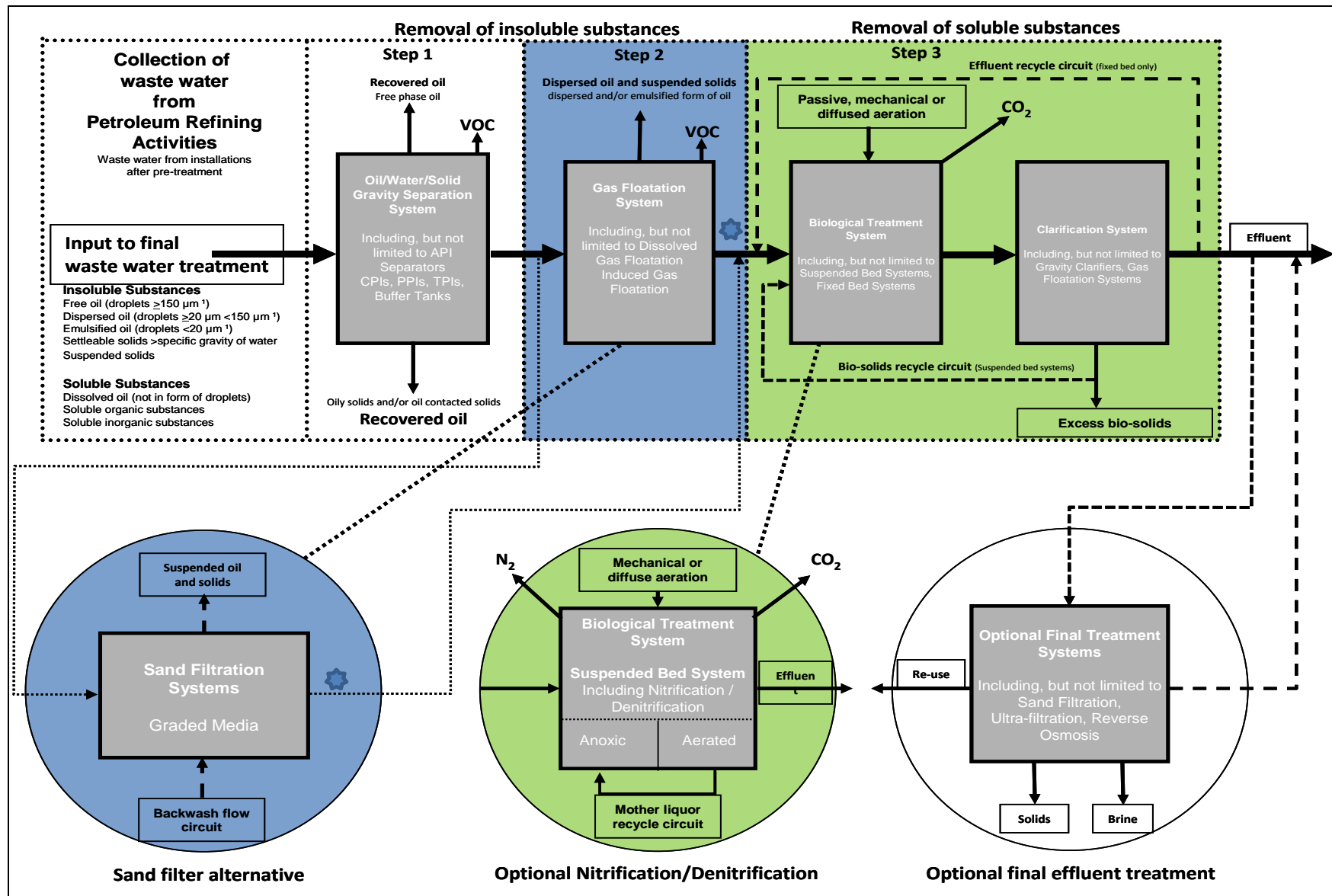


Figure 4.67: Process flow diagram of a typical refinery waste water treatment plant

4.24.1 Management of waste water within a refinery

This section gives some indication of what can be done in a refinery in terms of the management of waste water. In other words, indication will be given as to whether it is better to combine waste waters from different processes or whether it is better to process them independently in some independent waste water plant. Topics related to the storage of waste water are also included here. This section deals with process waste water, cooling water and sanitary waste water, ballast water, cleaning water, accidentally oil-contaminated water, continuously oil-contaminated water, etc.

Description

Some techniques to consider for improving the waste water treatment performance and efficiency are listed below.

- Apply process water integration (see Section 4.15.4.1), e.g. stripped sour water and sour water, as desalter wash water (stripped sour water only) or as wash water in the overhead FCC main column to reduce the process water flow to the effluent treatment plant.
- Apply water and drainage systems (see Section 4.15.4.2). Rainwater from polluted plant areas (storm water) should be collected and routed to a treatment plant. For collection, a 'first flush' scheme may be used that collects the more severely contaminated storm water and discharges subsequent precipitation directly. Non-contaminated water may be discharged directly or reused. It is necessary that the WWTP be able to handle high quantities of rainwater or that a sufficient buffer capacity is installed to prevent overloading. Use of equalising tanks for the storage of waste water.
- The temperature of the waste water is controlled or limited in order to preserve the performance of the biological treatment.
- Control of surfactants in waste water. Surfactants entering the refinery waste water streams will increase the amount of emulsions and sludges generated. They can enter the system from a number of sources, including: washing unit pads with detergents; treating gasolines with an end point over 200 °C, thereby producing spent caustics; cleaning tank truck interiors; and using soaps and cleaners for miscellaneous tasks. In addition, the overuse and mixing of the organic polymers used to separate oil, water and solids in the waste water treatment plant can actually stabilise emulsions. The use of surfactants needs to be minimised by educating operators, routing surfactant sources to a point downstream of the DAF unit and by using dry cleaning, high-pressure water or steam to clean surfaces of oil and dirt.

Achieved environmental benefits

Water stream integration and other water management techniques (see Section 4.15.4) aim at reducing the total volume of water used prior to discharge and especially saving high-quality potable and demineralised water.

Based on Section 3.24, the data on released waste water (2006 to 2008) for 44 European refineries with dedicated waste water treatment plants are the following:

- annual median (50th percentile) effluent volume: 2.9 million m³/year;
- range: 0.54 – 212 million m³/year;
- specific median (50th percentile) effluent volume: 0.44 m³/tonne throughput;
- range: 0.15 to 11.7 m³/tonne throughput.

Driving force for implementation

To reuse water, to reduce the hydrocarbon charge to the waste water treatment, and to reduce VOC emissions.

Reference literature

[160, Janson 1999], [168, VROM 1999], [178, HELPE 1999], [205, Jansson 2000], [207, TWG 2001].

4.24.2 Sour water stripping (SWS)

Sour water from the various refinery units is, for the most part, stripped in a SWS and can normally be reused together with the crude distillation unit overhead wash water as desalter wash water (see Figure 4.68). This is the main process water source in refineries.

Description

Single-stage stripping

Most sour water strippers are single-stage, requiring one stripping column. Figure 4.68 shows a typical single-stage sour water stripper. The sour water streams from the process units are collected in a sour water collection vessel. This provides both hold-up for feed and acts as a settler, where oil separation takes place. From this vessel, sour water is pumped via a feed/effluent exchanger, to the top of the stripper column. The sour water is countercurrently stripped in the column by steam, either injected live or generated in a reboiler. This column is usually refluxed to reduce the water content in the sour gas. Operating pressure in the column varies from 0.5 to 1.2 barg depending on the destination of the off-gas. When necessary, pH control is applied to maximise either H₂S or NH₃ removal.

Sour off-gases from a stripper unit can be routed either to a sulphur recovery unit (SRU), to an incinerator, or to the sour gas flare. Since off-gases directly routed to an incinerator or a flare can contribute very significantly to the overall refinery release of SO₂ (up to 40 %) and NO_x, routing to a SRU should be preferred and is now commonly practised with the exception of overhead gases from an air-stripped sour water stripper for safety reasons.

Two-stage stripping

The two-stage sour water stripper differs from the single-stage stripper by operating the first column at a lower pH (6) and, eventually, at a higher pressure (9 barg), removing H₂S over the top and NH₃/water via the bottom, and the second stage at a higher pH (10), removing the NH₃ over the top and a stripped water stream at the bottom. A well designed oil/water separation drum instead of a tank can also achieve the benefits of reduced hydrocarbons entering the sour water stripper. This results in:

- much lower H₂S and NH₃ concentrations in the stripped water;
- the possibility to send to the SRU only sour off-gases generated at the first stripping stage, which do not contain high NH₃ concentrations, known as a source of severe perturbation of the Claus reaction due to ammonium deposits.

Other techniques to consider are:

- Standby stripping facilities or additional storage to be provided for sour water. Duplication of the SWS.
- Sulphide-rich effluents streams should be stripped prior to discharge to effluent treatment. Most commonly, SWSs have a surge drum to remove entrained hydrocarbons that can cause upset in the downstream SRU.

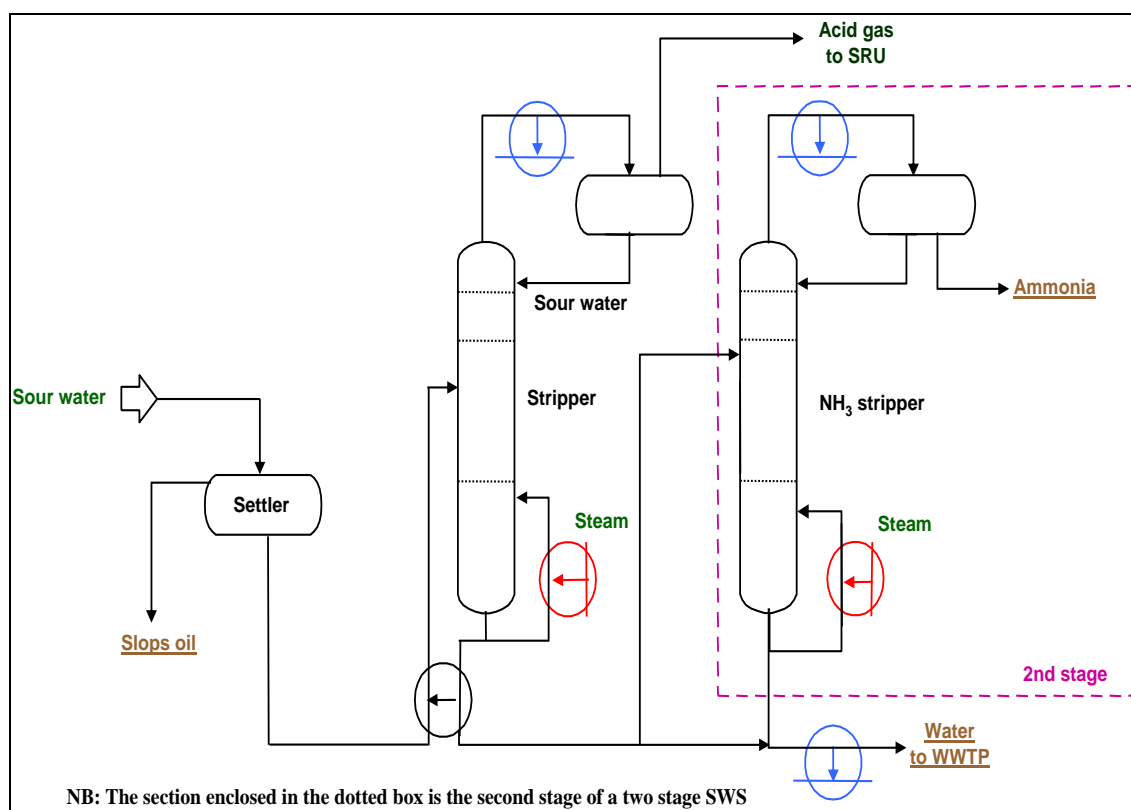


Figure 4.68: Simplified process flow diagram of a sour water stripping unit (SWS)

Achieved environmental benefits

Single-stage stripping

The SWS produces sour off-gas and stripped effluent which are routed to downstream units. The table below shows the achievable levels for a single-stage SWS.

| | Source | Flow | Composition min./max. | Comments |
|--|--|---|--|--|
| Emissions: sour gas | SWS off-gas to be routed to SRU | Plant-specific | Mainly H ₂ S and NH ₃ . Content depends on crude quality and refinery configuration | A two-stage stripping could allow the separation of sour gas in H ₂ S-rich and NH ₃ -rich streams, which can then be treated much more efficiently |
| Effluent: stripped sour water (SSW) | SWS effluent to be used as desalter wash water or routed to WWTP | 20 – 50 m ³ /h in a 5 Mt/yr refinery | COD: 500mg/l H ₂ S: 10 mg/ Phenol: 30 – 100 mg/l NH ₃ : 75 - 150 mg/l | SSW can be reduced by limiting live steam injection in process units and increasing the use of a reboiler |

Stripped sour water can be routed to the waste water treatment plant or, preferably, to the process units for reuse, after appropriate cooling if necessary. Normally, stripped sour water can be used as desalter wash water, provided its contaminant levels are adequate (NH₃ less than 150 ppm and H₂S less than 20 ppm). These limits are required to avoid corrosion in downstream units (i.e. CDU overhead system).

Two-stage stripping

In the first stage, H₂S is separated, whereas in the second one NH₃ is removed from water, and concentrated to a solution containing 10 % NH₃ which can be reused to reduce NO_x emissions. Example data of a typical two-stage stripping unit are given in Table 4.119.

Table 4.119: Performance of a two-stage sour water stripping unit in the Holborn refinery

| Parameters | Column 1 supply (mg/l) | Column 2 outlet (mg/l) | Final efflux after treatment by WWTP (mg/l) |
|--------------------|------------------------|------------------------|---|
| COD | 14 400 | 599 | 37 |
| Hydrocarbons | 98 | 4 | 1.1 |
| N tot. Inorg. | 1 373 | 6 | 7 |
| NH ₄ -N | 1 372 | 5 | 5 |
| Phenols | 182 | 141 | 0.1 |
| Sulphide | 1 323 | 5 | 0.5 |

The two-stage SWS process can achieve an overall H₂S and NH₃ recovery of 98 % and 95 % respectively associated with residual concentrations in the stripped waters in the respective ranges of 0.1 – 1.0 mg/l and 1 – 10 mg/l. Sulphide and ammonia loads to be treated in the WWTP are consequently much lower, helping to avoid the need for an additional stage dedicated to treatment (e.g. nitrification/denitrification).

Some level of nitrogen compounds is nevertheless needed in the refinery waste water as an essential nutrient for biological growth in biological waste water treatment.

Ammonia generated in the two-stage SWS process can be used within the refinery after appropriate pretreatment, in particular to reduce NO_x emissions (SNCR, see in particular Sections 4.5.4.2 and 4.23.3.2). For example, at the Holborn refinery (Germany), the reuse of the NH₃-rich effluent from such a SWS for a CO boiler achieves a reduction of NO_x of 180 t/yr, NH₄-N of 250 t/yr and solid waste from the WWTP of 10 %.

Sour water decantation and equalisation

The addition of a sour water tank of sufficient capacity homogenises the different water streams, further removes oil that may cause plugging in the stripper, and helps to produce acid gas of constant composition for the SRU. As less hydrocarbons enter the SRU, catalysts are better protected against the coking phenomenon, with favourable effects on SRU efficiency and reliability.

Cross-media effects

Routing the off-gases from the stripper unit to the SRU, especially in the case of a single-stage SWS, can negatively influence the efficiency and the running conditions of the SRU, mainly due to the NH₃ content in the gas. In the case of a two-stage SWS, the steam consumption increases significantly with the stripping capacity and pressure.

Operational data

| Electricity (kWh/t) | Steam consumed (kg/t) | Acid and caustic consumption |
|---------------------|-----------------------|------------------------------|
| 2 – 3 | 100 – 200 | NA |

Most commonly SWSs have a surge drum to remove entrained hydrocarbons, which could otherwise cause upsets in the downstream SRU. The SWS feed is normally preheated by feed/effluent exchangers to a tower inlet temperature of 100°C to save stripping steam. For a stripper operating at higher pressure, higher temperatures are tolerable. Nevertheless, a feed temperature which results in flashing of the feed in the feed line to the stripper tower is to be avoided.

Decreasing the water content in the off-gas below 30 mol % is not practised, as problems with salt deposition from the vapour phase can occur. This salt deposition particularly occurs when

CO₂ is present in the sour gas, and the level of corrosive ammonium bisulphide (NH₄HS) in the condensate refluxed to the stripper column increases beyond the level acceptable from a materials and corrosion perspective.

The use of a second stripping column consumes extra chemicals for pH control (acid, caustic) and extra energy.

Applicability

Two-stage stripping: if the SWS bottoms are not reused but are sent to biotreating they may still contain too much NH₃. In order to solve this in the SWS unit, the SWS column can either be equipped with a larger number of stages or a two-stage stripper can be installed (see section enclosed in dotted box in Figure 4.68). In the case of retrofitting for a two-stage stripper, an existing SWS can be converted to sour water concentrators to reduce its size. The more or less pure ammonia stream from the second stripper top might be sent to the CO boiler of the FCC unit for NO_x reduction purposes or to the hot flue-gas of a furnace.

Economics

In a French refinery, an existing single-stage low-pressure SWS was upgraded in 2010 by adding a new high-pressure stage (9 barg - 180°C - 30 t/h) dedicated to H₂S removal. The expected investment cost is EUR 24.8 million, obviously much higher than the cost range for a low-pressure stage.

Other data for different sour water strippers are shown in Table 4.120.

Table 4.120: Economics and performance of sour water strippers

| Year built | Design NH ₃ effluent conc. (mg/l) | Actual performance (mg/l NH ₃) | Design flow rate (m ³ /h) | Capital cost (EUR million) | Operating cost/yr (EUR 10 ³) |
|------------|--|--|--------------------------------------|----------------------------|--|
| 1996 | 18 | | 22 | 2.7 | – |
| 1996 | 10 | | 30 | 4.0 | 21 |
| 1992 | Max. 150 | 13 | 20 | 0.6 | 97 |
| 1993 | 50 | | 25 | 5.4 | 43 |
| 1995 | 50 | 35 | 32 | 5.3 | 175 |
| 1992 | 100 | | 50 | 10.9 | – |

Driving force for implementation

Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia and hydrogen sulphide) that will be contaminated with hydrocarbons and/or steam condensate. Sour water needs stripping prior to further treatment or reuse as wash water. A typical composition of the sour water is 900 mg/l of hydrogen sulphide, 2 000 mg/l ammonia, 200 mg/l phenols and 15 mg/l hydrogen cyanide.

Example plants

Two-stage stripping is seldom applied in refineries. In the Holborn refinery in Germany, a two-stage SWS is integrated as an alternative to an effluent denitrification stage in the WWTP. Also, in the new TOTAL Mitteldeutschland refinery, a two-stage SWS unit has been installed. The company Total has operated one at Feyzin refinery since 2008 (with a high-pressure single stage).

Reference literature

[148, Irish EPA 1993], [166, CONCAWE 1999], [168, VROM 1999], [171, UN/ECE 1998], [182, Ecker 1999], [183, HP 1998], [200, Gilbert 2000], [222, UBA 2000], [228, TWG 2000].

4.24.3 Reduction and recovery of hydrocarbons from waste water at source

Description

Generally benzene, phenols and hydrocarbons in waste water can often be treated more easily and effectively at the point where they are generated rather than at the waste water treatment plant after mixing. Consequently the identification of hydrocarbon sources is the first measure to consider. The techniques described below as possible options have been identified by a number which is then used throughout this section. More information is available for each technique in the CWW BREF [6, COM 2003].

- Technique 1: Nitrogen or air stripping for benzene recovery from waste water. Nitrogen stripping can be used to strip benzene and other low aromatic compounds from waste water. The mixture is treated by activated carbon beds that capture the organics, allowing cleaned nitrogen to recycle to the waste water stripper. Periodically, the carbon bed is regenerated in situ with live steam: desorbed organic vapours are carried by the steam to a condenser and are subsequently decanted into organic and water layers. Organics are returned to the refinery as valuable feed.
- Technique 2: Liquid-liquid extraction from waste waters for phenol extraction from waste water using a countercurrent extraction column. After distillation, the solvent (e.g. butyl acetate) is recycled back to the extraction column.
- Technique 3: High-pressure wet air oxidation (>20 barg). Water is intensively mixed with air and organic compounds are oxidised in the presence of a catalyst at high temperature and high pressure (250 °C, 7 MPa). Sulphur-containing substances are oxidised to sulphates; amines and nitriles are converted to molecular nitrogen; ammonia will require a biological or physical treatment step. More information is available in the CWW BREF [6, COM 2003].
- Technique 4: Low-pressure oxidation (<20 barg). Persistent organic compounds are treated with oxygen and are mineralised in a biological treatment plant (BOC gases).

Achieved environmental benefits

- Technique 1: A refinery uses this system to reduce 1 895 l/d of waste water containing 50 ppm of benzene, 100 ppm of toluene/xylenes and 100 ppm of other hydrocarbon liquids. The recovery unit consistently reduced benzene to below 500 ppb. About 35 000 kg of hydrocarbon liquid are returned to the refinery feedstock annually. This technique can also be applied to remove MTBE.
- Technique 2: Recoveries greater than 99 % or raffinate concentrations well below 1 ppm can be achieved. With this technique, waste water containing >1 % phenols was treated to get purified water with a phenol content lower than 1 ppm (efficiencies: higher than 99 %; Koch Process Technology, Inc.). Phenol-containing waste water may also be treated microbiologically.
- Technique 3: Abatement efficiency can be 99 % [6, COM 2003].
- Technique 4: Efficiency can be in the range 60 – 90 % [6, COM 2003].

Operational data

- Technique 1: Nitrogen stripping has several advantages over air: oxygen does not reduce biological fouling of the stripper and nitrogen reduces the risk of refinery upsets creating explosive mixtures in the recovery unit.
- Technique 2: Typical utilities consumption per m³ water feed are:
 - electricity: 159 kWh;
 - steam (20.7 barg): 15.6 kg;
 - steam (2.07 barg): 103 kg;
 - water tempered at 45 °C ($\Delta T = 19$ °C): 5.6 m³;
 - water cooling at 29 °C ($\Delta T = 11$ °C): 2.5 m³.

Applicability

- Technique 1: This technology is used for the treatment of desalting water and waste water from BTEX plants (Texaco Development Co; AMCEC, Inc.)
- Technique 2: They can be designed to handle waste water streams with phenol levels from several hundred ppm to saturation (approximately 7 %) and above.

Economics

- Technique 1: Design and equipment supply costs of around USD 1 250 000. Annual utility costs are around USD 85 000.
- Technique 2: Cost-effective for levels of phenols higher than 1 %. A base case example for a waste water stream of 27.2 m³/h containing 6 % phenol was treated with 4.3 m³/h solvent in a four-column system. The overall phenol recovery was 99.3 %.
 - Investment, extractor only: USD 1.32/m³.
 - Complete system: USD 3.43/m³.
 - Recovered value: USD 3.96/m³.

Driving force for implementation

Reduction and recovery of hydrocarbons.

Example plants

- Technique 1: More than 15 systems ranging from 800 l/min to 12 000 l/min are now operating in various US refineries. Air stripping for the removal of MTBE has been used successfully in at least one European refinery.
- Technique 2: This system is typically applied when phenol concentrations are high. This type of system treats waste water for a US resin producer.

Reference literature

[4, Hydrocarbon Processing 1998], [6, COM 2003], [182, Ecker 1999], [228, TWG 2000], [233, L. Helm, C. Spencer, et al.1998].

4.24.4 Primary treatment - Removal of insoluble substances

Waste water collection

The collection of waste water from the various units after any specific process treatment can be considered part of the global waste water treatment. Actually, a waste water treatment plant (WWTP), especially with a biological step, operates most effectively under constant conditions (pH, hydraulic load or flow rate) and pollutant load or concentrations.

To buffer the WWTP operation against short-term (e.g. daily) and long-term (e.g. weekly) variations, equalisation facilities are in place, either decentralised at the various production installations or centrally in or near the WWTP. The buffering and retention volumes also allow analysis to check compatibility of the waste water influent with the subsequent treatment. Flow and load/concentration balancing are also referred to as equalisation, buffering or homogenisation. More information on this pretreatment step is available in the CWW BREF [6, COM 2003].

Process water coming from the SWS is one of the main process water sources in refineries. Moreover, some incompatible process effluents and drains from off site (flares and tanks) add to the total flow of process water. This effluent has to pass first an oil/water separator (CPI, PPI or API) for free oil and solids removal and an equalisation tank, where sometimes further oil skimming can be accomplished.

4.24.4.1 Step 1 - Oil removal

Description

The purpose of this step is the separation and extraction of insoluble hydrocarbons. These techniques rely on the principle of the difference in gravity between the phases (liquid – liquid or solid – liquid): the phase with the higher density will settle and the one with lower density will float to the surface.

Step 1 may generally include:

- API separators (APIs);
- corrugated plate interceptors (CPIs);
- parallel plate interceptors (PPIs);
- tilted plate interceptors (TPIs);
- buffer and/or equalisation tanks.

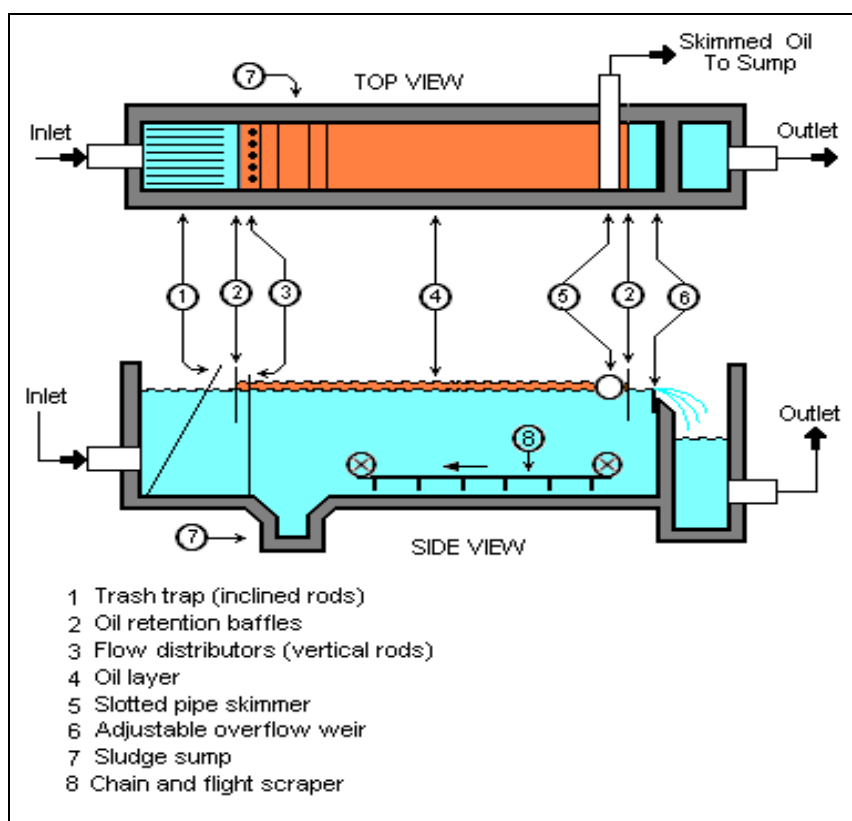


Figure 4.69: API separator general description

Internal corrugated plates used in CPIs, PPIs and TPIs reduce the residence time required to achieve separation of the insoluble hydrocarbons targeted for removal and, therefore, reduce the required separation system compared to APIs.

These techniques aim at achieving separation and extraction of free oil droplets generally greater than or equal in size to 150 μm .

The water phase exiting these separation systems will generally contain insoluble dispersed oil droplets, emulsified oil droplets, suspended solids, soluble oil not in the form of droplets, soluble inorganic substances, soluble organic substances, and trace amounts of insoluble free phased hydrocarbon and settleable solids.

Accumulations of viscous and/or semi-solid hydrocarbon materials with little fluid characteristics may not be effectively removed by gravity flow using a fixed position overflow skimming pipe. Flexible skimming devices may be applied to improve oil removal. Close operator monitoring and intervention on demand may be necessary to extract viscous and/or semi-solid hydrocarbon material accumulation on the surface using manual measures.

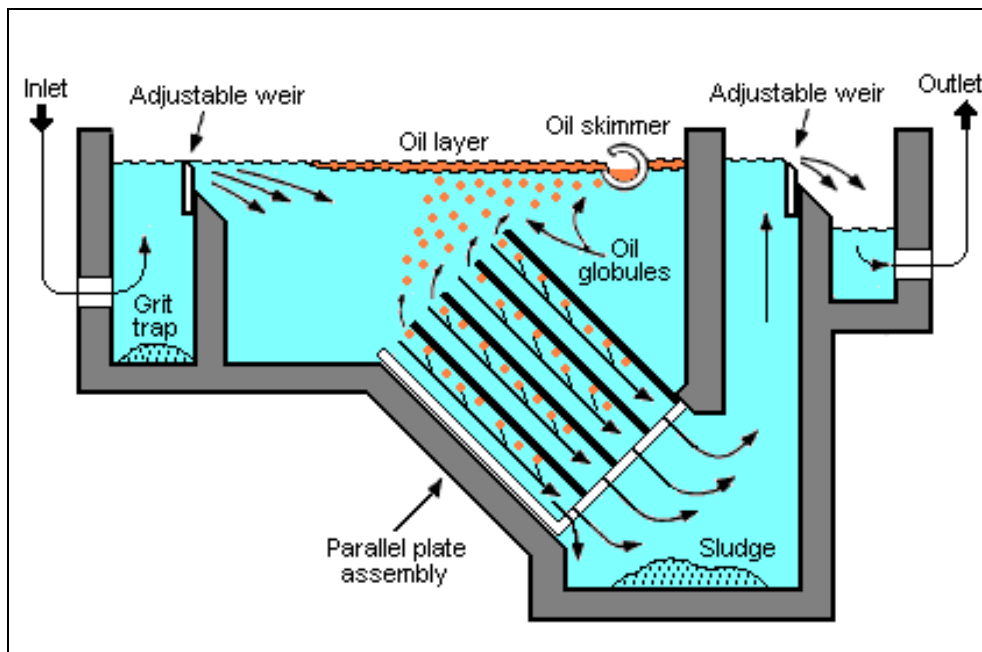


Figure 4.70: Parallel plate separator (PPI) general description

Achieved environmental benefits

The performance of CPIs and APIs, as regards oil removal, suggest 50 – 100 ppm oil in the outlet.

Cross-media effects

Separators operating with internal corrugated plates are susceptible to solids fouling.

These systems may not be equipped with internal mechanical solids extraction systems or internal mechanical oil extraction systems. Systems not equipped with internal mechanical solids extraction systems may be at risk of solids accumulation and eventual plate pack fouling from the bottom up, if accumulated solids cannot be effectively removed through either the gravity drain and/or pump-out techniques.

Systems not equipped with internal mechanical oil extraction systems may be at risk of hydrocarbon accumulation on the surface of the water phase.

When separators are not covered they can lead to VOC emissions.

Operational data

No detailed data.

Applicability

These systems are fully applicable. CPIs are easier to cover than APIs. Retrofitting to existing separators may be complicated depending on structural design, type of mechanical oil skimmers and solid scrapper systems used, and position of electrical drivers. Due to VOCs and air inside the covered area, the API may operate above the lower explosive limit; if so, significant modifications may be needed.

Economics

Table 4.121 shows some reported examples of costs for API separators units.

Table 4.121: Examples of costs for API units

| Year built | Type | Capacity (m ³ /h) | Capital cost (EUR x 10 ⁶) | Operating cost/yr (EUR x 10 ³) | Comments |
|------------|------|------------------------------|---------------------------------------|--|---|
| 2011 | API | 750 | 8.825 | | Replacement of API separator with floating roof tanks |
| 1962 | | 600 | - | 330 | Operating costs for 2010 |
| 1966 | | 187 | - | 148 | Operating costs for 2011 |
| 2010 | | 300 | 0.694 | | |
| 2011 | | 1 100 | 8.500 | | Estimation for a new API unit |

Source: [120, CONCAWE 2012]

Driving force for implementation

Maximising the collection of oil. It has been estimated that between 0.5 % and 4 % of the crude oil processed in a refinery can be found in the waste water before any treatment, depending on the complexity of a refinery. Consequently, oil is always recovered from the drainage system before the waste water is passed for final treatment.

Example plants

Well proven technologies of 44 refinery sites in the TWG sample data collection with dedicated WWTPs, of which 42 reported having one separator, and among them 11 were covered. See detailed figures in Table 4.125. Separators have been progressively covered in a growing number of European refineries.

Reference literature

[48, TOTAL 2010], [119, CONCAWE 2011], [160, Janson 1999], [166, CONCAWE 1999], [171, UN/ECE 1998], [191, UBA Austria 1998], [201, Manduzio 2000].

4.24.4.2 Step 2 - Further oil/water/solid separation

Description

This further step requires the use of chemicals to improve the solid/liquid or liquid/liquid separation of the remaining hydrocarbons and suspended solids in the waste water stream after the first treatment step. An injection of coagulant or flocculant is necessary to trap the oil droplets and the suspended solids that passed the first treatment. In order to improve the flocculation, a pH adjustment may be required prior to it.

Techniques for this treatment step may include:

- dissolved gas flotation (DGF);
- induced gas flotation (IGF);
- sand filtration.

DGF and IGF are the same techniques as Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF) used in other industrial sectors, where air bubbles enable the flocculated solids to float. But as potentially explosive vapours may accumulate, the pressurisation system uses gases instead of air to reduce risks.

DGF and IGF techniques aim at achieving the separation and extraction of free oil droplets generally less than 150 µm in size, emulsified oils and suspended solids. The sludge formed is

brought to the water surface by flotation, whereby tiny gas bubbles are also captured by the sludge flocs. The sludge is skimmed off and the water is routed to the next treatment step. Sand filtration (or dual-media) is an alternative process to flotation. Clarifiers may also be an alternative.

For all these separation techniques, the size of the flocs entering the separation step is crucial. Only flocs over several μm will be stopped. If the flocculation is not efficient, oil and particles will pass through the process. The water phase exiting this step will generally contain soluble oil not in the form of droplets, soluble inorganic substances, soluble organic substances, and trace amounts of free oil droplets, dispersed oil droplets, settleable and suspended solids.

Another technique to consider for this step is the treatment of the DAF float separately, rather than sending it to the slop oil system.

Achieved environmental benefits

Flotation units achieve 10 – 20 ppm of oil and prepare the waste water to improve the biological treatment results.

Cross-media effects

The techniques may lead to VOC and HC emissions. See Section 4.24.7 for odour reduction.

Operational data

Chemicals utilisation includes acid and/or alkali for pH correction, and FeSO_4 or FeCl_3 for coagulant requirements or a polyelectrolyte for the flocculation units. In practice, pH correction and polymer dosing to the flocculation flotation unit need daily attention and fine-tuning. The energy requirement for the WWTP is relatively low; the aeration compressor being the largest consumer.

Applicability

Fully applicable.

Economics

Table 4.122 shows some reported examples of costs for flotation units.

Table 4.122: Examples of costs for flotation units

| Year built | Type | Design flow rate (m^3/h) | Capital cost ($\text{EUR} \times 10^6$) | Operating cost/yr ($\text{EUR} \times 10^3$) |
|------------|------|--|---|--|
| 1995 | DAF | 80 | 0.2 | 18 |
| 1994 | DAF | 300 | 1.4 | 20 |
| 1989 | IAF | 400 | 2.4 | 47 |
| 1993 | DAF | 350 | 8.0 | 683 |
| 1996 | IAF | 818 | 0.4 | 112 |
| 1996 | DAF | 50 | 3.1 | – |
| 1996 | DAF | 800 | 1.5 | – |
| 2009 | DAF | 500 | 6.3 | 250 |
| 2010 | | 250 | 1.5 | 182 ⁽¹⁾ |
| 2009 | | 100 | 1.7 | 207 |

⁽¹⁾ Based upon an average cost of 12 % per year of capital investments.
Source: Data 2009-2010 CONCAWE

Driving force for implementation

To reduce the hydrocarbon and solids content in the waste water.

Example plants

Well proven technologies of 44 refinery sites from the TWG sample data collection with dedicated WWTP, of which 40 reported having one flocculation step (mainly DAF type) and two reported the use of a sand filter. See detailed figures in Table 4.125.

Reference literature

[48, TOTAL 2010], [112, CONCAWE 2011], [164, Noyes 1993], [166, CONCAWE 1999].

4.24.4.3 Step 3 - Biological treatment**Description**

Step 3 aims at biological assimilation of the soluble hydrocarbons, inorganic substances and organic substances still contained in the water phase after the previous treatment steps. Insoluble substances contained in the water phase exiting Step 2 may also be subject to biological assimilation.

Biological treatment techniques may include:

- fixed bed systems;
- suspended bed systems.

One of the most commonly used suspended bed systems in refinery WWTPs is the activated sludge process. Fixed bed systems may be, for example, the biofilter or trickling filter.

By using these techniques, soluble substances are removed from the waste water through the process of adsorptive contact with the biomass, followed by absorption into the biomass and assimilation of the soluble substances. This assimilation results primarily in new biomass growth and carbon dioxide emissions from the biomass respiration process.

The biomass maintained in the bioreactor is typically a mixture of naturally occurring microorganisms, that are acclimated to assimilating the soluble substances in the waste water.

A clarification step may be necessary to separate the biomass solids from the biologically contacted waste water prior to discharge to the environment.

Suspended bed biological treatment systems can be configured for biological nitrification/denitrification.

VOC emissions during aeration can be minimised by replacing shallow aeration turbines with air (or oxygen) dosing devices at the bottom of the aeration basin.

Nitrification/denitrification

If deep nitrogen removal is required, denitrification in a biotreater is an option. Through this system, biological nitrification occurs with oxygen where ammonia-nitrogen is oxidised to nitrite (with *Nitrosomonas* bacteria) and then to nitrate (*Nitrobacter*). Subsequent biological denitrification of nitrate to nitrogen gas takes place under anoxic conditions and in the presence of a carbon source (heterotrophic bacteria).

Other techniques to consider are as follows:

- Heterotrophic denitrification, usually combined with autotrophic sulphide oxidation (the reductive potential of sulphide is used to eliminate nitrogen via denitrification. Simultaneously, sulphide is oxidised, so that sulphide precipitation in subsequent biological treatment units is unnecessary).
- Use of granular activated carbon (GAC). Pollutants are adsorbed and biologically treated in an oxygen-rich atmosphere (attainable COD: <100 mg/l).

- Use of powdered activated carbon (PAC, similar to GAC).
- Macro-porous polymer extraction (MPPE) which can be placed upstream of the biological treatment plant. It uses porous polymer beads containing an immobilised extraction liquid. Based on the high affinity of the hydrocarbon components for this liquid, phenols, BTEX, PAH, etc. can be removed.
- Covering of the waste water treatment plant. Fixed covers have to be designed taking into account loss prevention purposes (build-up of explosive vapours).

In addition, emissions to air of VOCs (including benzene) and odorous components (hydrogen sulphides and mercaptans) are not uncommon and cannot always be fully controlled by upstream measures.

Safety aspects (i.e. the explosiveness of VOC-air mixtures) are also to be considered, however they are less dangerous than in upstream units.

Achieved environmental benefits

A biotreater can remove 80 – 90 % of dissolved oil and COD, as well as 90 – 98 % of BOD, under normal operating conditions. Natural nitrogen removal is normally about 10 % in an activated sludge unit (ASU), 70 – 80 % in a nitrification/denitrification biotreater (DNB) and up to 90 % in a tertiary (add-on) denitrification unit. For MAH/phenol, >95 % removal can be achieved based on a well-adapted biological system. Oxygen aeration in activated sludge plants can be up to 50 % more efficient than air aeration techniques.

Cross-media effects

Energy consumption, activated carbon wastes when GAC or PAC is applied and methanol consumption (for heterotroph bacteria) when denitrification is applied. Waste water treatment generates sludge. If waste water treatment is not properly operated, the amount of sludge can be increased.

Operational data

If a denitrification biotreater is applied, pumping energy is relatively high. If a tertiary treatment unit is used for ammonia removal by biological nitrification, methanol can be used in a subsequent denitrification stage as an oxygen receptor for denitrifying bacteria. In some refineries, biotreaters' powdered activated carbon is dosed for meeting discharge specifications. The sensitivity of a biotreater against shock loads (peak discharges) of toxic compounds (e.g. sulfolane, MTBE, phenol, cyanide, sulphide) is relatively high and should be avoided. Methods to consider include spill prevention measures, appropriate procedures, good housekeeping and the equalisation of influent in a buffer tank.

Applicability

Fully applicable, bearing in mind that toxic or inhibitory streams should not enter a biotreater.

A restriction for nitrification is reported in cases of existing activated sludge systems with a low sludge residence time (average sludge lifetime below 15 – 20 days). A low sludge residence time in existing biological sludge systems is typically caused by a high ratio of organic load to amount of biomass.

For additional information, the CWW BREF [6, COM 2003] provides input concentration thresholds for a list of substances that are toxic to a biological activated sludge process and substances that are likely to inhibit a biological nitrification/denitrification process. Furthermore, other inhibitors to nitrification other than those referred to in the CWW BREF should be considered: ammonium and nitrite, sulphides, benzene and phenols.

Ammonium and nitrite

Ammonium and nitrite can slow down nitrification, mainly in their non-dissociated forms (NH₃ and HNO₂). The effects of ammonium and of nitrite on the *Nitrosomonas* and *Nitrobacter*

bacteria species, which are the ones mostly involved in the biological nitrification activity, are a function of the concentrations and pH values as shown in Figure 4.71.

Nitrosomonas, responsible for the degradation of ammonium into nitrite, are inhibited at concentrations of free ammonia between 10 mg/l and 150 mg/l. *Nitrobacter*, in turn, degrade nitrite in nitrate but are inhibited at concentrations of free ammonia between 0.1 mg/l and 1 mg/l.

When *Nitrobacter* are inhibited, non-dissociated nitrite can have a retro-effect on *Nitrosomonas* at concentrations between 0.2 and 2.8 mg/l, which causes nitrification to stop almost entirely.

When the active sludge is acclimated, nitrification will take place even if the concentration of ammonia or nitrous acid is higher than the limit values listed above. Concentrations of 10 mg/l $\text{NO}_2\text{-N}$ are not expected to cause problems during nitrification.

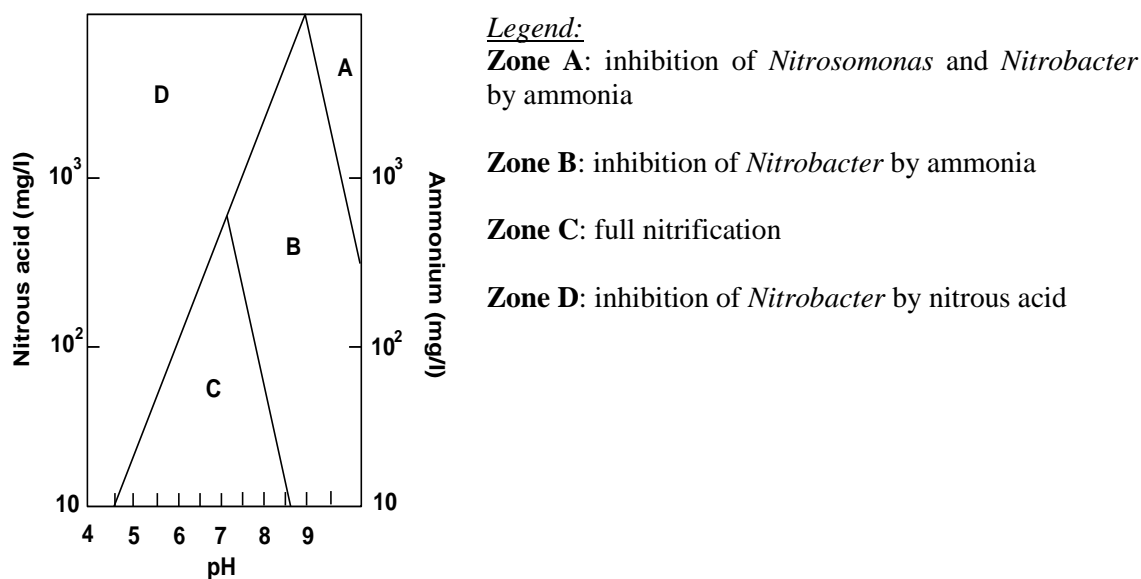


Figure 4.71: Nitrification tolerance of *Nitrosomonas* and *Nitrobacter* species

Sulphides

The biological nitrification processes need very low concentrations of heavy metals in complex forms. However, sulphurous compounds are strong inhibitors of nitrification, as they have a chelating effect which limits the availability of these heavy metals. Sulphide itself can already inhibit the nitrification at concentrations as low as 0.5 mg/l, leading to a strong reduction of the activity of nitrifying bacteria.

Benzene and phenol

In favourable conditions, an aerobic WWTP is able to cope with concentrations of phenols up to 400 mg/l without any effect on the active sludge. However, high phenol concentrations and phenol peaks are toxic for nitrifying bacteria. Benzene is less toxic for nitrifying bacteria than phenol. However, *Nitrosomonas* have an enzyme which can oxidise benzene into phenol, and consequently increase the substrate toxicity. In Table 4.123, some concentration levels associated with their inhibition effects are reported.

Table 4.123: Inhibition effects of phenol and benzene on biological nitrification

| Concentration | Degree of inhibition (1) | Reference |
|--|--|-----------------------|
| Phenol | | |
| 20 mg/l | IC50 <i>Nitrosomonas</i> | Blum en Speece (1991) |
| 5 – 6 mg/l | IC75 in active sludge | Dyreborg (1995) |
| 4 – 10 mg/l | Minimum inhibition limit value | Eysenbach (1994) |
| 3 mg/l | IC50 | Juliastuti (2003) |
| 50 mg/l | Complete inhibition | |
| 100 mg/l | Acclimatisation of sludge by gradually raising the concentration | Stafford (1974) |
| Benzene | | |
| 13 mg/l | IC50 <i>Nitrosomonas</i> | Blum en Speece (1991) |
| NB: IC50 = the concentration of an inhibitor that is required for 50 % inhibition of its target. | | |

According to many sources, mainly peak concentrations are really problematic for nitrification, but can be partially solved by installing enough upstream buffering capacity.

Economics

Examples of recent cost data for biotreatment

In France, a recently (2009 – 2010) installed 5 000 m³ aeration tank biotreater, treating 450 m³/h, was built for EUR 18 million (costs including only building and installation of the basin).

Two other examples of re-engineered WWTPs are provided in Table 4.124.

Table 4.124: Example of costs for waste water treatment plants at a refinery site

| Site reference and description | Units | Capacity | Capital cost (EUR million) | Comments |
|---|--|-------------------------|----------------------------|----------------|
| CONCAWE 1 Re-engineering of WWTP system 2003 to 2005 | DAF (2 units) | 750 m ³ /h | 8.860 | 4.430 per unit |
| | Bioreactor (Biox design) | 1 000 m ³ /h | 5.565 | |
| | Sludge management system | - | 2.970 | |
| | DAF VOC recovery system | - | 0.084 | |
| | Total units costs | | 17.479 | |
| | Total project costs (Investments, design, labour) | | | 40.000 |
| CONCAWE 2 Re-engineering of WWTP system 2005 | Existing DAF upgrade | NA | 2.000 | 2 units |
| | Bioreactor (Biox) upgrade | NA | 2.000 | |
| | Storm water collection tank | | 1.000 | |
| | Total units costs | | 5.000 | |
| | Total project costs | | | NA |

Source: CONCAWE 2011

Driving force for implementation

Removal of dissolved organic compounds by biological treatments.

Denitrification biotreaters are usually applied in environments sensitive to nitrates.

Example plants

Well proven technologies of 44 refineries (2008 TWG data collection), of which 30 reported using an activated sludge technique, 8 reported using a biofilter or a trickling filter technique. In

addition, 12 refineries reported a nitrification or denitrification step technique. See detailed figures in Table 4.125.

Nitrification/denitrification biotreater installations are operational at least at Harburg and Rheinland (DE) and Gothenburg (SE) refineries, and an anoxic reactor is in operation at Antwerp (BE).

An MPPE unit (Macro-Porous Polymer Extraction) is installed at the Kollsnes and Ormen Lange gas plant (NO) for reducing organic components in the process water.

Anqing refinery (China) is to operate in 2012 a 1 000 m³/h powdered activated carbon treatment unit combined with biological treatment in order to reuse 500 m³/h of water from this site.

The current use of waste water techniques in refineries has been investigated in 2008 through a CONCAWE survey [112, CONCAWE 2011] whose results are in the following tables.

Table 4.125: Type of waste water treatment reported by refineries (CONCAWE survey 2008)

| Treatment type | Number of sites | Type of biological treatment | Number of sites |
|------------------------|-----------------|------------------------------|-----------------|
| Three-stage biological | 103 | Activated sludge | 78 |
| | | Trickling filter | 16 |
| | | Aerated lagoon | 5 |
| | | Non-aerated lagoon | 1 |
| | | Fixed bed biofilm reactor | 1 |
| | | Aerated tank | 1 |
| | | Other | 1 |
| Mechanical | 2 | | |
| Chemical | 2 | | |
| Physical | 4 | | |
| API separator | 0 | | |
| External WWTP | 14 | | |
| Total | 125 | | |

A study carried out by a Norwegian refinery, in 2005, to compare the MPPE and the Activated Carbon (AC) adsorption processes applied in a gas refinery showed the following costs.

Table 4.126: Costs of two waste water treatment processes at a gas refinery in Norway

| Process | Capital cost (EUR million) | Operating cost/yr (EUR 10 ³) |
|---------------------------------|----------------------------|--|
| Macro-Porous Polymer Extraction | 0.5 – 0.6 | 130 |
| Activated Carbon | 0.26 – 0.39 | 39 |

NB: Cost estimated from conversion ratio (2005) of NOK 1 = EUR 0.128 9.

Reference literature

[4, Hydrocarbon Processing 1998], [16, Polders 2009], [112, CONCAWE 2011], [151, Sema, Sofres 1991].

4.24.5 Additional treatments

In countries where water is a scarce resource, it is sometimes economically attractive to further improve the quality of the effluent in order to reuse the water as cooling water or even as a source for the preparation of boiler feed water (BFW), provided the pressure level of steam will allow the make-up. In that case, sand filtration (SF) and/or ultrafiltration (UF) followed by activated carbon filtration (AC) and/or reverse osmosis (RO) for salt removal generates sufficiently pure water for entering the demineralisation unit of the BFW preparation unit. Other techniques are ozonation/oxidation, ion exchange, and incineration.

Description

Techniques for the reduction of the salt contents of the waste water include: ion exchange, membrane processes or osmosis. Metals may be separated by precipitation, flotation, extraction, ion exchange or vacuum distillation.

Achieved environmental benefits

See Section 4.24.6.

Cross-media effects

Energy consumption, wastes and concentrates from exhausted activated carbon, membranes and metal sludges.

Operational data

When activated carbon is applied as an adsorbent, it must be regenerated or replaced at set intervals depending on the functioning of the system.

Economics

When the WWTP is extended with SF and AC, the operating costs of the resulting WWTP is doubled compared with a WWTP without these systems (base case). With UF and RO, both the investment costs and the operating costs will approximately triple those of the base case.

Driving force for implementation

Applied in refineries where shortages of water supply may occur.

Example plants

Sand filters, ultrafiltration, activated carbon and reverse osmosis are proven technologies in many industrial sectors. For the refinery sector, dealing with large volumes of effluent, sand filtration is possible. From the 2008 TWG data collection, among the 44 refineries sampled the following breakdown treatment steps were reported.

Table 4.127: Techniques reported for WWTPs within the 2008 TWG data collection

| Treatment type | Number of sites reporting | Techniques reported as used at this step | Number of sites ⁽¹⁾ | % use of the technique |
|-------------------------|---------------------------|--|--------------------------------|------------------------|
| First step | 44 | API | 37 | 84 % |
| | | CPI | 7 | 16 % |
| | | Buffering-Equalisation | 21 | 48 % |
| Second step | 44 | DAF | 30 | 68 % |
| | | IAF | 4 | 9 % |
| | | Flocculation/Flotation | 5 | 11 % |
| | | Sand filtration | 4 | 9 % |
| | | <i>None or not identified</i> | 3 | 7 % |
| Third step (biological) | 44 | Activated sludge | 27 | 61 % |
| | | Trickling filter | 1 | 2 % |
| | | Biofilter | 11 | 25 % |
| | | <i>None or not identified</i> | 4 | 9 % |
| Additional step | 44 | Sand filtration | 9 | 20 % |
| | | Lagoon | 4 | 9 % |
| | | Miscellaneous ⁽²⁾ | 9 | 20 % |
| | | <i>No final treatment</i> | 22 | 50 % |

⁽¹⁾ Various techniques may be reported for same site.
⁽²⁾ For the additional step, miscellaneous includes oxidation pond, clarification, decantation and DAF or IAF.
Source: [TWG data collection questionnaires]

Reference literature

[4, Hydrocarbon Processing 1998]

4.24.6 Global refinery waste water treatment performance

Description

This section deals with emission values that can be achieved, individually or in combination, by today's waste water treatment in refineries. The waste water system considered contains the various treatment steps, including the optional final one as shown in Figure 4.67 and as reported in Table 4.127 through the details of the 2008 TWG data collection.

Achieved environmental benefits and environmental performance

Ranges of release levels expressed in concentration on a yearly average basis are displayed in Table 4.128 and are considered to be achievable for the key water parameters typically used to characterise a release to water from a refinery which is using a good combination of techniques as described in this section. Specific load values are shown here as indicative parameters, as they are strongly dependent on the complexity or the type of refinery. These ranges suppose, in particular, that the treatment capacity of each treatment step is well adapted to the actual effluent load (average and peak regimes) received at the WWTP. Depending on the nitrogen intake, the lowest range limits for nitrogen compounds would require the use of a specific denitrification/nitrification stage.

Table 4.128: Reported ranges of emissions to water (50th percentiles) in dedicated WWTPs - 2008 TWG data collection

| Parameter | Reported concentration (mg/l) (yearly average) | Indicative corresponding load (g/tonne crude oil or feedstocks processed) (yearly average) |
|---|--|--|
| Maximum temperature | 30 – 35 °C | |
| pH | 6.5 - 8.5 | |
| Total suspended solids (TSS) (dried @ 105 °C) | <5 – 15 | 1 – 5 |
| Total organic carbon (TOC) | 5 – 15 | 1 – 5 |
| Total hydrocarbon oil content THC (EN 9977-1 or EN 9977-2) | <0.1 – 1 | <0.1 – 0.5 |
| Biological oxygen demand BOD (5 day ΔTU @ 20 °C) | 2 – 10 | 0.5 – 3 |
| Chemical oxygen demand COD (2 hour) | <30 – 60 | <10 – 25 |
| Ammoniacal nitrogen (as N) | 0.25 – 2.5 | 0.1 - 1 |
| Nitrites (as N) | <0.05 – 0.2 | 0.05 – 0.1 |
| Nitrates (as N) | <0.5 – 2 | 0.2 – 1 |
| Kjeldahl nitrogen (as N) | <2 – 5 | 1 – 2.5 |
| Total nitrogen (as N) | 2 – 10 | 0.5 – 3 |
| Cyanides | 0.003 – 0.01 | 0.001 – 0.005 |
| Fluor (refineries using HF alkylation) | <0.2 – 2 | <0.25 – 1 |
| Phosphates (as P) | 0.1 – 0.5 | 0.05 – 0.15 |
| Total P (as P) | 0.05 – 0.5 | 0.05 – 0.15 |
| Sulphides | 0.005 – 0.05 | 0.002 – 0.02 |
| Sulphite | <2 | |
| AOX (as Cl) | <0.1 – 0.2 | <0.01 – 0.06 |
| Benzene | <0.001 – 0.005 | <0.001 – 0.002 |
| Polycyclic aromatic hydrocarbons (PAH-16) | <0.000 1 – 0.001 | <0.000 1 – 0.000 3 |
| BTEX | <0.001 – 0.005 | 0.001 – 0.005 |
| MTBE (lower levels for refineries not producing MTBE) | <0.001 – 0.01 | 0.001 – 0.005 |
| Phenols | 0.01 – 0.1 | 0.001 – 0.02 |
| Tensioactives (ionic and anionic) | <0.5 | |
| Heavy metals (Cd+ Cr+ Cu+ Hg+ Mn+ Ni+ Pb+ Se+ Sn+ V+ Zn) | 0.05 – 0.2 | 0.02 – 0.1 |
| As | <0.001 – 0.003 | <0.000 1 – 0.001 |
| Cd | <0.001 – 0.005 | <0.000 1 – 0.001 |
| Total Cr | <0.001 – 0.003 | <0.000 1 – 0.001 |
| Cr (VI) as Cr | <0.001 – 0.002 | <0.000 1 – 0.001 |
| Co | <0.001 – 0.003 | <0.000 1 – 0.001 |
| Zn | <0.005 – 0.05 | <0.001 – 0.02 |
| Pb | <0.000 1 – 0.001 | <0.000 1 – 0.005 |
| Fe | 0.15 – 0.5 | 0.01 – 0.2 |
| Cu | 0.003 – 0.05 | <0.001 – 0.02 |
| Ni | 0.002 – 0.05 | <0.001 – 0.02 |
| Hg | <0.000 1 – 0.000 5 | <0.000 1 – 0.001 |
| V | <0.005 – 0.02 | <0.001 – 0.005 |

NB: Levels given within this table are indicative ranges derived from the TWG 2008 data collection (38 sites with dedicated WWTPs - yearly averages data and main graphs are provided in Section 3.1.3) and based on a 50th percentile calculation applied independently to each pollutant.

Source: [207, TWG 2001] Updated with TWG data collection questionnaires (2008).

Table 4.129: Reported emissions to water observed in 98 EU refineries (2010 survey)

| Parameter | Concentration weighted annual average per refinery (mg/l) | | | Relative load (g/tonne throughput) | | |
|--|---|----------------------|----------------------|---------------------------------------|-----------------------|----------------------|
| | 5th percentile | 95th percentile | Average | 5th percentile | 95th percentile | Average |
| Biological Oxygen Demand - BOD (5d) | 0.17 | 26.68 | 8.62 | 0.49 | 36.61 | 11.83 |
| Chemical Oxygen Demand - COD (2h) | 2.67 | 149.00 | 59.00 | 6.81 | 270.00 | 106.35 |
| Total Organic Carbon - TOC | 0.06 | 38.30 | 13.62 | 0.03 | 38.82 | 15.94 |
| Total Suspended solids | 0.46 | 117.35 | 63.09 | 1.09 | 315.53 | 180.54 |
| Oil in Water (OiW) or Total Petroleum Hydrocarbons index (TPH) | 0.04 | 6.24 | 1.83 | 0.02 | 10.78 | 2.68 |
| Benzene | 0.00 | 0.11 | 0.02 | 0.00 | 0.07 | 0.02 |
| Toluene | 0.00 | 0.09 | 0.02 | 0.00 | 0.07 | 0.02 |
| Ethylbenzene | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 |
| Xylenes | 0.00 | 0.22 | 0.03 | 0.00 | 0.18 | 0.02 |
| Phenol index | $3.50 \cdot 10^{-4}$ | 0.36 | 0.08 | $1.71 \cdot 10^{-4}$ | 0.38 | 0.08 |
| MTBE | $1.00 \cdot 10^{-5}$ | 0.20 | 0.05 | $2.06 \cdot 10^{-6}$ | 0.21 | 0.08 |
| Naphthalene | 0.00 | $1.71 \cdot 10^{-3}$ | $9.50 \cdot 10^{-4}$ | 0.00 | $2.94 \cdot 10^{-3}$ | $1.17 \cdot 10^{-3}$ |
| Anthracene | 0.00 | $2.68 \cdot 10^{-4}$ | $6.33 \cdot 10^{-5}$ | 0.00 | $2.42 \cdot 10^{-4}$ | $7.49 \cdot 10^{-5}$ |
| Fluoranthrene | 0.00 | $4.44 \cdot 10^{-4}$ | $8.13 \cdot 10^{-5}$ | 0.00 | $3.53 \cdot 10^{-4}$ | $8.92 \cdot 10^{-5}$ |
| Benzo(a)pyrene | 0.00 | $1.46 \cdot 10^{-4}$ | $3.34 \cdot 10^{-5}$ | 0.00 | $1.73 \cdot 10^{-4}$ | $4.70 \cdot 10^{-5}$ |
| Benzo(b)fluoranthrene | 0.00 | $1.00 \cdot 10^{-4}$ | $4.49 \cdot 10^{-5}$ | 0.00 | $7.75 \cdot 10^{-4}$ | $1.33 \cdot 10^{-4}$ |
| Benzo(k)fluoranthrene | 0.00 | $2.03 \cdot 10^{-5}$ | $4.45 \cdot 10^{-6}$ | 0.00 | $1.93 \cdot 10^{-5}$ | $5.94 \cdot 10^{-6}$ |
| Benzo(g, h, i)perylene | 0.00 | $2.40 \cdot 10^{-4}$ | $9.96 \cdot 10^{-5}$ | 0.00 | $6.81 \cdot 10^{-4}$ | $2.09 \cdot 10^{-4}$ |
| Indeno(1, 2, 3 ^c d)pyrene | 0.00 | $9.82 \cdot 10^{-5}$ | $2.69 \cdot 10^{-5}$ | 0.00 | $1.18 \cdot 10^{-4}$ | $3.74 \cdot 10^{-5}$ |
| Dichloromethane | 0.00 | $3.51 \cdot 10^{-3}$ | $2.47 \cdot 10^{-3}$ | 0.00 | $2.03 \cdot 10^{-02}$ | 0.01 |
| Trichloromethane | 0.00 | $8.69 \cdot 10^{-3}$ | $1.22 \cdot 10^{-3}$ | 0.00 | $4.23 \cdot 10^{-3}$ | $1.22 \cdot 10^{-3}$ |
| Pentachlorobenzene | 0.00 | $5.20 \cdot 10^{-3}$ | $1.51 \cdot 10^{-3}$ | 0.00 | $5.38 \cdot 10^{-3}$ | $1.57 \cdot 10^{-3}$ |
| Ammonia | 0.00 | 10.39 | 2.71 | 0.00 | 12.97 | 3.14 |
| Ammoniacal Nitrogen | 0.01 | 13.82 | 3.12 | 0.04 | 12.31 | 3.04 |
| Chlorides | 0.35 | 2628.31 | 548.25 | 0.10 | 4119.30 | 641.41 |
| Fluorides | 0.00 | 5.07 | 1.23 | 0.00 | 3.38 | 0.93 |
| Free cyanides | 0.00 | 0.08 | 0.02 | 0.00 | 0.06 | 0.02 |
| Kjeldahl Nitrogen | 0.02 | 22.44 | 6.36 | 0.02 | 9.85 | 3.79 |
| Nitrates | $6.23 \cdot 10^{-4}$ | 34.56 | 8.15 | 0.00 | 28.99 | 7.08 |
| Nitrites | 0.02 | 3.56 | 0.77 | 0.00 | 3.23 | 1.33 |
| Sulphides | 0.00 | 0.23 | 0.08 | 0.00 | 0.33 | 0.08 |
| Sulphites | 0.00 | 32.73 | 7.31 | 0.00 | 155.51 | 34.56 |
| Total Nitrogen | 0.10 | 30.32 | 8.92 | 0.49 | 20.71 | 9.02 |
| Total Phosphorus | 0.01 | 1.81 | 0.55 | 0.03 | 1.51 | 0.48 |
| Arsenic | 0.00 | 0.02 | 0.01 | 0.00 | 0.03 | 0.01 |
| Cadmium | 0.00 | 0.01 | $1.83 \cdot 10^{-3}$ | 0.00 | 0.01 | $3.04 \cdot 10^{-4}$ |
| Chromium | 0.00 | 0.02 | 0.01 | 0.00 | 0.03 | 0.01 |
| Chromium (VI) | 0.00 | 0.05 | 0.02 | 0.00 | 0.08 | 0.02 |

| Parameter | Concentration weighted annual average per refinery (mg/l) | | | Relative load (g/tonne throughput) | | |
|-----------|---|-----------------|----------------------|---------------------------------------|----------------------|----------------------|
| | 5th percentile | 95th percentile | Average | 5th percentile | 95th percentile | Average |
| Cobalt | 0.00 | 0.01 | $2.55 \cdot 10^{-3}$ | 0.00 | 0.02 | $3.05 \cdot 10^{-3}$ |
| Copper | 0.00 | 0.04 | 0.01 | 0.00 | 0.03 | 0.01 |
| Iron | 0.01 | 1.49 | 0.42 | 0.006 359 66 | 2.70 | 0.56 |
| Lead | 0.00 | 0.03 | 0.01 | 0.00 | 0.03 | 0.01 |
| Mercury | 0.00 | 0.00 | $4.38 \cdot 10^{-4}$ | 0.00 | $1.31 \cdot 10^{-3}$ | $4.60 \cdot 10^{-4}$ |
| Nickel | $6.17 \cdot 10^{-5}$ | 0.09 | 0.02 | $2.1579 \cdot 10^{-5}$ | 0.08 | 0.02 |
| Selenium | 0.00 | 0.05 | 0.02 | 0.00 | 0.05 | 0.02 |
| Vanadium | 0.00 | 0.15 | 0.04 | 0.00 | 0.13 | 0.03 |
| Zinc | $1.35 \cdot 10^{-3}$ | 0.21 | 0.06 | $1.08 \cdot 10^{-3}$ | 0.22 | 0.06 |

Source: CONCAWE 2010 Effluent Survey in [254, CONCAWE 2012]

In addition, another data-set on water emissions has been made available by CONCAWE (Report 10/3) for spot sample campaign measurements (ESP survey 2008 – 2009), including 105 refineries in Europe. From direct discharging sites (90 % of the entire refineries sample), the following ranges are reported for a number of parameters (Table 4.130).

Table 4.130: Reported emissions from spot sample campaign measurements with direct discharge (ESP survey 2008 – 2009)

| Parameter | Concentration range (mg/l) | 5th percentile (mg/l) | Median 50th percentile | Average (mg/l) ⁽¹⁾ | 75th percentile (mg/l) | 95th percentile (mg/l) | Limit of quantification (LoQ) mg/l |
|---|--|-----------------------|------------------------|-------------------------------|------------------------|------------------------|------------------------------------|
| Total hydrocarbon content (Oil in Water) ⁽²⁾ | 0.05 – 24 | 0.05 | 0.18 | 1.55 | 1.40 | 11 | 0.05 |
| COD | 16 – 391 | 23 | 48 | 61 | 78 | 135 | 10 |
| BOD | 1 – 130 | 1 | 4 | 8 | 9 | 23 | 3 |
| Kjeldahl N | 1 – 83 | 1 | 3.4 | 7 | 10 | 26 | 1 |
| Cadmium (Cd) | $2 \cdot 10^{-3}$ – $40 \cdot 10^{-3}$ | $3.5 \cdot 10^{-3}$ | $21 \cdot 10^{-3}$ | $21 \cdot 10^{-3}$ | $30 \cdot 10^{-3}$ | $38 \cdot 10^{-3}$ | $1 \cdot 10^{-3}$ |
| Lead (Pb) | $7 \cdot 10^{-3}$ – $12 \cdot 10^{-3}$ | $7 \cdot 10^{-3}$ | $9 \cdot 10^{-3}$ | $9 \cdot 10^{-3}$ | $11 \cdot 10^{-3}$ | $12 \cdot 10^{-3}$ | $4 \cdot 10^{-3}$ |
| Mercury (Hg) | $0.02 \cdot 10^{-3}$ – $2 \cdot 10^{-3}$ | $0.039 \cdot 10^{-3}$ | $0.095 \cdot 10^{-3}$ | $0.3 \cdot 10^{-3}$ | $0.4 \cdot 10^{-3}$ | $1.5 \cdot 10^{-3}$ | $0.02 \cdot 10^{-3}$ |
| Nickel (Ni) | $5 \cdot 10^{-3}$ – $460 \cdot 10^{-3}$ | $6 \cdot 10^{-3}$ | $12 \cdot 10^{-3}$ | $35 \cdot 10^{-3}$ | $24 \cdot 10^{-3}$ | $106 \cdot 10^{-3}$ | $5 \cdot 10^{-3}$ |
| Vanadium | $3 \cdot 10^{-3}$ – 1.7 | $6 \cdot 10^{-3}$ | $13 \cdot 10^{-3}$ | $60 \cdot 10^{-3}$ | $28 \cdot 10^{-3}$ | $104 \cdot 10^{-3}$ | $5 \cdot 10^{-3}$ |
| Benzene | $0.2 \cdot 10^{-3}$ – 0.630 | $2.4 \cdot 10^{-3}$ | $2 \cdot 10^{-3}$ | $51 \cdot 10^{-3}$ | $11 \cdot 10^{-3}$ | $238 \cdot 10^{-3}$ | $0.2 \cdot 10^{-3}$ |

⁽¹⁾ For average calculation, <LoQ has been replaced by LoQ.
⁽²⁾ Oil in Water: measurements carried out by GC-FID method compatible with EN9377-2. LoQ 0.05 mg/l.
Source: [122, CONCAWE 2010]

Operational data

Effluent treatment units are designed so that the most important key parameters (suspended solids, TOC, COD and BOD) of the final discharge stream can be appropriately monitored in order to ensure efficient treatment. The specific constraints of each parameter analysis are to be taken into account, e.g. TOC and COD may be monitored continuously whereas BOD needs several days for the analysis.

Examples of two data-sets based on short-term averaging periods (daily or monthly) for COD emissions for one entire year appear in Figure 4.72 and Figure 4.73. Additional data from a CONCAWE survey including 50 data-sets from 30 refineries (some data-sets for the same site and different years) with short-term (mainly daily) and long-term values have been gathered and their results are presented in Table 4.132 and Figure 4.74 to Figure 4.84.

From these data, it is possible to observe the variation of the daily or monthly averages against the reported yearly averages.

Table 4.131: Examples of variation in emissions to water

| Site | Parameter (Unit) | Yearly average | Daily average variation | Monthly average variation | Observations |
|-------|------------------|--------------------------|--------------------------------|--------------------------------|----------------------------------|
| FR-01 | COD (mg/l) | Avg. = 82 (Med. = 84) | [56 % - 156 %] ⁽¹⁾ | [66 % - 123 %] ⁽³⁾ | Based on daily data |
| FR-02 | COD (mg/l) | Avg. = 50 | [50 % - 240 %] ⁽²⁾ | [79 % - 137 %] ⁽³⁾ | Based on monthly aggregated data |
| FR-01 | TSS (mg/l) | Avg. = 8 | [25 % - 215 %] ⁽¹⁾ | [51 % - 190 %] ⁽³⁾ | Based on daily data |
| FR-02 | TSS (mg/l) | Avg. = 11 | [17 % - 235 %] ⁽²⁾ | [52 % - 87 %] ⁽³⁾ | Based on monthly aggregated data |

(¹) Expressed as a range: [5th percentile/yearly average - 95th percentile/yearly average].
(²) Expressed as a range: [Minimum data/yearly average - Maximum data/yearly average].
(³) Expressed as a range: [Min. monthly average/yearly average - Max. monthly average/yearly average].

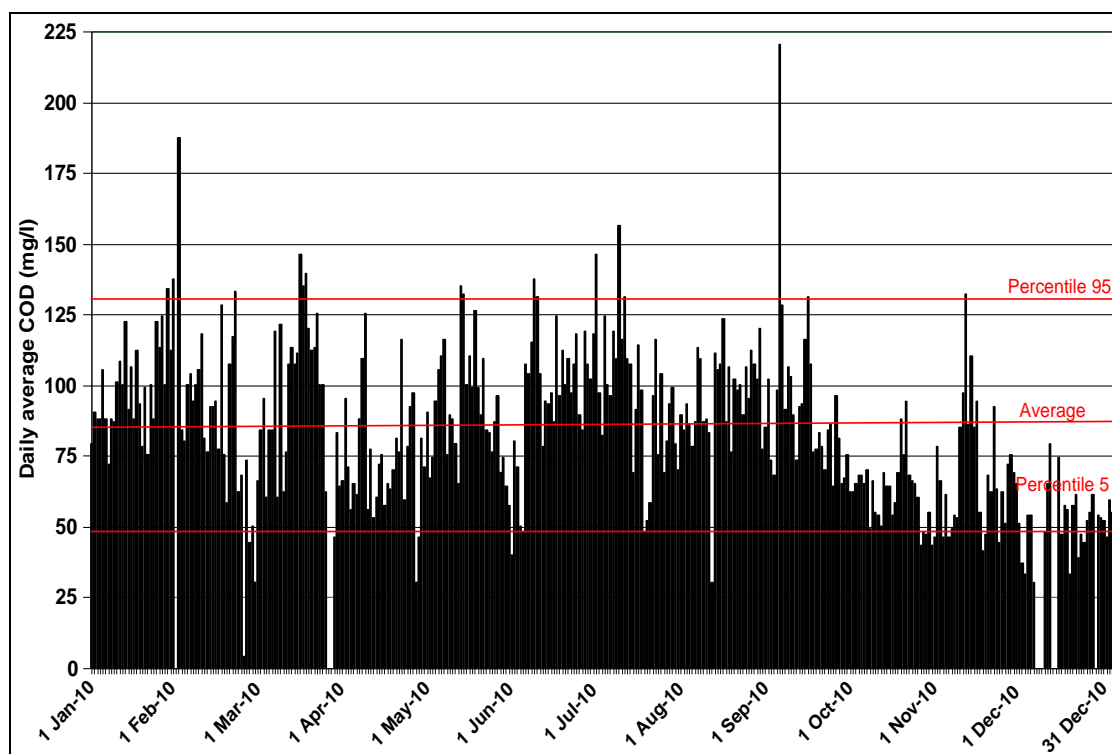


Figure 4.72: Daily COD concentration variations from one refinery site (FR-01)

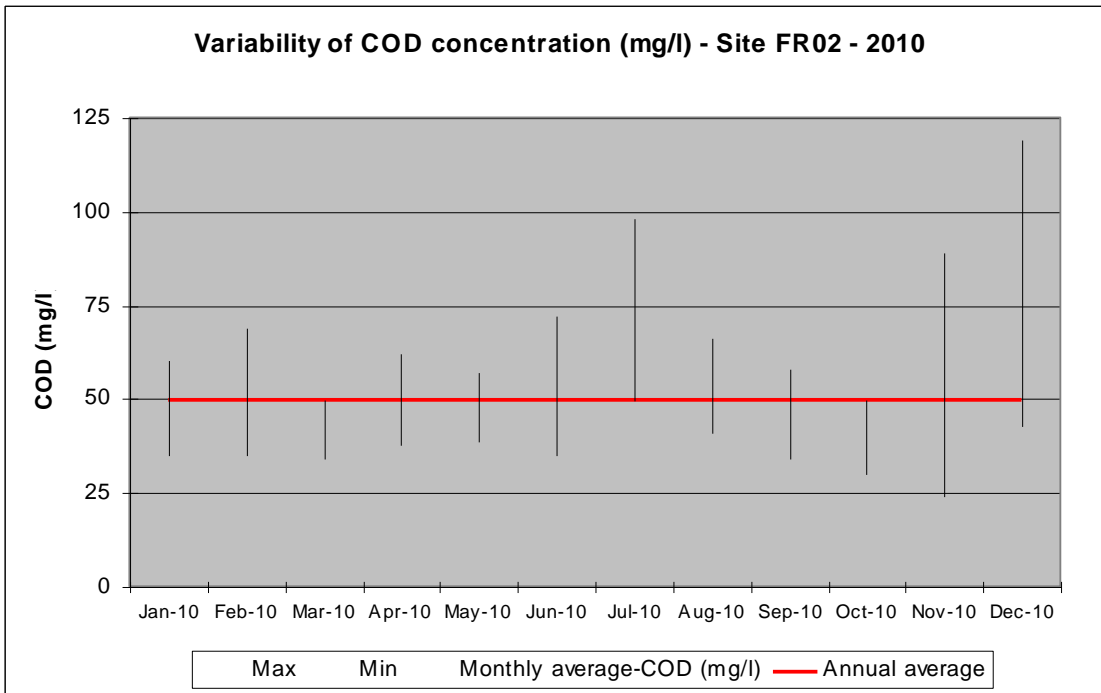


Figure 4.73: Monthly COD concentration variations from one refinery site (FR-02)

Table 4.132: Results from 50 data-sets from 30 refinery sites for COD, TSS and TPH

| Parameter | COD | | | TSS | | | TPH | | |
|-------------------------------------|-----------------|--------------------|-------------------|----------------|--------------------|-------------------|-----------------|--------------------|-------------------|
| | Yearly Average | Max./average Ratio | P95/average Ratio | Yearly Average | Max./average Ratio | P95/average Ratio | Yearly Average | Max./average Ratio | P95/average Ratio |
| Site 1-2010 | 49.61 | 2.40 | 1.43 | 7.87 | 8.64 | 2.16 | 1.26 | 9.30 | 1.43 |
| Site 2-2010 | 84.44 | 2.61 | 1.52 | 11.84 | 2.87 | 1.82 | 1.50 | 3.90 | 1.00 |
| Site 3-2009 | 67.75 | 3.69 | 1.67 | 14.19 | 8.74 | 2.47 | 3.243 | 15.42 | 2.78 |
| Site 3-2010 | 48.40 | 4.59 | 1.94 | 7.86 | 5.34 | 2.16 | 1.525 | 7.15 | 1.97 |
| Site 3-2011 | 50.84 | 13.26 | 2.20 | 7.47 | 8.04 | 2.68 | 1.117 | 19.69 | 2.40 |
| Site 4-2009 | 189.96 | 3.81 | 1.86 | 45.81 | 2.05 | 1.64 | 11.31 | 2.74 | 1.87 |
| Site 4-2010 | 157.55 | 3.22 | 1.86 | 37.51 | 4.19 | 2.01 | 4.38 | 4.11 | 2.81 |
| Site 4-2011 | 175.82 | 3.56 | 2.24 | 37.20 | 2.63 | 2.01 | 1.29 | 10.07 | 1.01 |
| Site 5-2009 | 42.52 | 2.82 | 1.41 | 10.56 | 3.88 | 2.00 | 1.17 | 7.70 | 1.71 |
| Site 5-2010 | 49.23 | 5.36 | 1.45 | 11.20 | 8.84 | 2.05 | 1.19 | 4.22 | 2.53 |
| Site 5-2011 | 48.34 | 2.88 | 1.65 | 12.13 | 5.36 | 2.47 | 1.34 | 39.16 | 2.83 |
| Site 6-2009 | 90.74 | 3.06 | 1.64 | 27.77 | 2.88 | 2.26 | 5.40 | 5.19 | 1.48 |
| Site 6-2010 | 95.64 | 2.31 | 1.56 | 23.98 | 3.71 | 2.72 | 5.23 | 2.87 | 1.34 |
| Site 6-2011 | 84.42 | 2.19 | 1.47 | 20.52 | 3.22 | 1.93 | 5.34 | 3.37 | 1.31 |
| Site 7-2009 | 55.82 | 1.79 | 1.42 | 16.60 | 5.96 | 2.00 | NA | NA | NA |
| Site 7-2010 | 48.82 | 4.04 | 1.47 | 15.74 | 8.83 | 2.22 | NA | NA | NA |
| Site 7-2011 | 52.48 | 6.02 | 1.56 | 16.10 | 10.56 | 2.17 | NA | NA | NA |
| Site 8-2011 | 29.24 | 2.02 | 1.40 | NA | NA | NA | 0.60 | 3.16 | 2.33 |
| Site 9-2010 | 100.52 | 5.19 | 1.63 | 23.90 | 9.08 | 2.21 | 1.34 | 39.16 | 2.83 |
| Site 10-2010 | 86.12 | 4.41 | 1.51 | 13.29 | 5.57 | 2.46 | 3.00 | 1.98 | 1.00 |
| Site 11-2010 | 34.16 | 5.39 | 2.01 | 8.04 | 11.19 | 2.24 | 0.21 | 25.27 | 3.12 |
| Site 12-2011 | 93.39 | 5.25 | 2.13 | 45.70 | 6.47 | 2.30 | 0.74 | 15.43 | 2.85 |
| Site 13-2011 | 106.42 | 8.53 | 2.44 | 46.88 | 14.84 | 2.86 | 2.73 | 8.10 | 2.13 |
| Site 14-2011 | 93.17 | 2.63 | 2.25 | 25.28 | 2.85 | 1.99 | NA | NA | NA |
| Site 15-2011 | 45.51 | 2.99 | 1.49 | 4.17 | 10.41 | 2.41 | 0.21 | 8.13 | 2.39 |
| Site 17-2009 | NA | NA | NA | 29.40 | 3.98 | 1.83 | NA | NA | NA |
| Site 17-2010 | NA | NA | NA | 41.18 | 7.77 | 1.96 | NA | NA | NA |
| Site 17-2011 | NA | NA | NA | 36.75 | 4.43 | 2.07 | NA | NA | NA |
| Site 18-2009 | 67.92 | 4.53 | 2.51 | 19.43 | 6.48 | 2.82 | NA | NA | NA |
| Site 18-2010 | 52.57 | 16.74 | 2.49 | 26.95 | 6.68 | 2.15 | NA | NA | NA |
| Site 18-2011 | 47.03 | 5.70 | 2.51 | 19.03 | 4.36 | 2.30 | NA | NA | NA |
| Site 19-2009 | 70.28 | 2.06 | 2.02 | 9.67 | 3.93 | 3.81 | 1.58 | 6.15 | 5.39 |
| Site 19-2010 | 78.20 | 1.89 | 1.85 | 11.99 | 3.25 | 2.87 | 1.54 | 6.17 | 3.37 |
| Site 19-2011 | 90.98 | 1.63 | 1.62 | 14.03 | 2.71 | 2.42 | 2.94 | 3.30 | 3.09 |
| Site 20-2010 | 47.08 | 2.70 | 1.33 | 0.06 | 16.72 | 0.84 | 0.14 | 8.29 | 2.07 |
| Site 21-2010 A | NA | NA | NA | 7.41 | 4.68 | 2.47 | NA | NA | NA |
| Site 21-2010 B | 59.60 | 1.73 | 1.32 | 15.12 | 1.79 | 1.78 | 0.38 | 18.57 | 2.51 |
| Site 22-2010 A | 34.14 | 2.90 | 1.64 | 14.91 | 17.44 | 2.55 | 0.16 | 8.71 | 2.64 |
| Site 22-2010 B | 64.65 | 2.00 | 1.53 | NA | NA | NA | 0.92 | 3.26 | 2.44 |
| Site 23-2011 | 43.87 | 1.82 | 1.41 | NA | NA | NA | 0.16 | 3.14 | 2.25 |
| Site 25-2011 | 46.47 | 1.72 | 1.44 | 8.58 | 7.57 | 3.26 | 0.33 | 5.99 | 2.89 |
| Site 26-2010 | 153.85 | 3.25 | 1.95 | 27.54 | 2.76 | 2.13 | 0.44 | 1.59 | 1.59 |
| Site 26-2011 | 146.53 | 3.82 | 1.50 | 26.24 | 2.06 | 1.84 | 0.40 | 1.94 | 1.90 |
| Site 27-2011 | 44.31 | 5.55 | 1.69 | 17.13 | 2.63 | 1.98 | 1.54 | 5.40 | 2.27 |
| Site 28-2010 | 31.88 | 2.07 | 1.83 | NA | NA | NA | 0.77 | 2.02 | 1.69 |
| Site 29-2010 | 61.14 | 3.11 | 1.60 | 13.04 | 3.30 | 1.98 | 0.55 | 11.19 | 2.93 |
| Site 30-2010 | NA | NA | NA | NA | NA | NA | 0.58 | 5.69 | 2.07 |
| Site 32-2010-1 | 39.56 | 1.87 | 1.24 | NA | NA | NA | 0.17 | 9.24 | 2.31 |
| Site 32-2010-2 | 65.57 | 1.89 | 1.48 | 21.56 | 3.94 | 1.67 | 0.13 | 1.60 | 1.60 |
| Site 33-2011 | 41.63 | 1.44 | 1.25 | NA | NA | NA | NA | NA | NA |
| Nb values | 45 | 45 | 45 | 43 | 43 | 43 | 38 | 38 | 38 |
| Median | 59.60 | 2.99 | 1.62 | 16.10 | 4.68 | 2.16 | 1.18 | 6.07 | 2.29 |
| Average | 72.63 | 3.83 | 1.72 | 19.81 | 6.11 | 2.23 | 1.76 | 8.90 | 2.27 |
| Range | 29 – 190 | 1.4 – 16.7 | 1.2 – 2.5 | 0 – 47 | 1.8 – 17.4 | 0.8 – 3.8 | 0.1 – 11 | 1.6 – 39.2 | 1 – 5.4 |
| Standard deviation | 38.97 | 16.74 | 0.35 | 11.95 | 17.44 | 0.48 | 2.18 | 9.04 | 0.82 |
| Coefficient of variation (%) | 54 % | 75 % | 21 % | 60 % | 63 % | 21 % | 124 % | 101 % | 36 % |

NB: Data are daily measurements reported from sites monitoring (except for both COD, TSS weekly at sites 19, 20, 21, 27, 28, 33- for TSS weekly at sites 6, 25, 26 - for TPH weekly at sites 4, 15, 20, 21, 22, 23, 25, 32 – TPH monthly at site 26).
All refineries operating a 3-step waste water treatment plant on site.
(°) Coefficient of variation is the standard deviation/average expressed as %.
Source: [255, CONCAWE 2012]

Assessment of daily variability and use of P95/AA ratio

It is reported that daily variability is strongly dependent on local factors, such as unexpected crude changes, periodic activities upstream of the treatment (e.g. purges, cleaning, operational unit changes), or weather conditions, that may interfere with the WWTP performance [255, CONCAWE 2012].

The daily variability may be due to:

- normal variations of WWTP efficiency;
- normal variations of input streams to the WWTP;
- other than normal operating conditions (OTNOC) of the entire system (production units and WWTP).

In order to assess these daily average fluctuations (from the data presented in Table 4.132 for COD, TSS and TPH) and to compare them to the annual average, the following ratios can be used:

- *the maximum/annual average ratio (MAX/AA)*: this is in a wide range (1.5 – 17) for both COD and TSS or even 1.5 – 39 for TPH;
- *the 95th percentile/annual average ratio (P95/AA)*: this is in a more narrow range (1.2 – 2.5) for COD, (0.8 – 3.8) for TSS, and (1 – 5.4) for TPH. For COD, TSS and TPH, the average is close to 2, with a limited coefficient of variation (21 % for both COD and TSS, 36 % for TPH).

These observations point to the use of the P95/AA ratio as an appropriate tool to assess the daily variability of a determinate data-set.

Based on the observed the data provided (see Table 4.132) and examples of analysis of possible causes for variations of the emissions concentration after the WWTP, it appears that in more than half of the reported cases, the value of the P95/AA ratio is less than 2 for both COD and TSS. For TPH, in more than half of the cases, the value of the P95/AA is less than 2.5 (see Figure 4.74, Figure 4.75 and Figure 4.76).

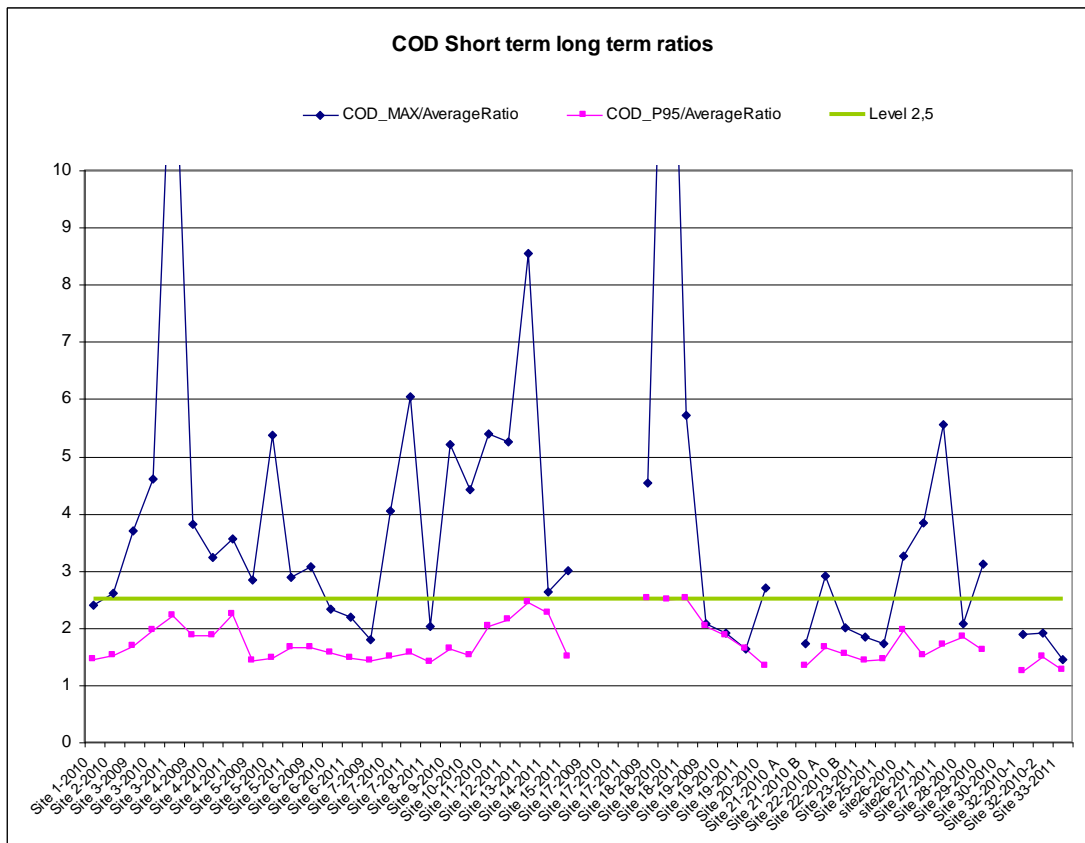


Figure 4.74: Assessment of daily variability of COD concentrations

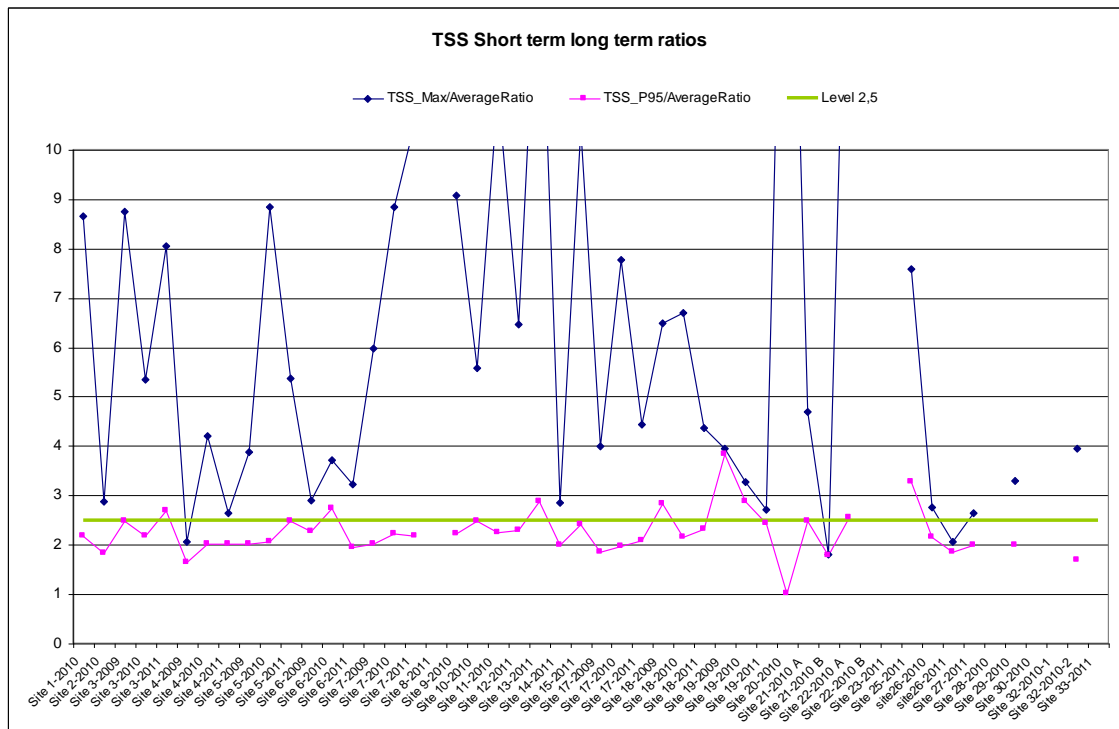


Figure 4.75: Assessment of daily variability of TSS concentrations

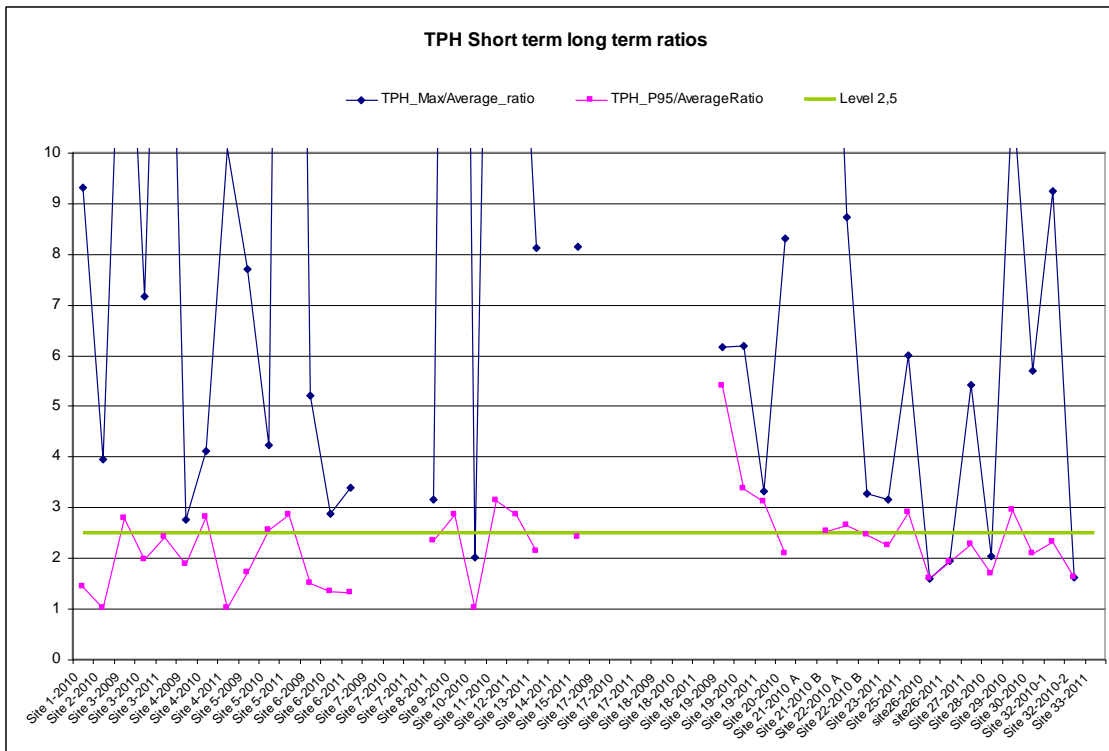


Figure 4.76: Assessment of daily variability of TPH concentrations

Influence of other than normal operating conditions on daily fluctuations of COD and TSS

The following graphs (see Figure 4.77 and Figure 4.78) show an example of a long time span (three years) data-set for COD and TSS, where some particular events are reported, e.g. unit start-up, incident, acclimatisation of biology treatment step.

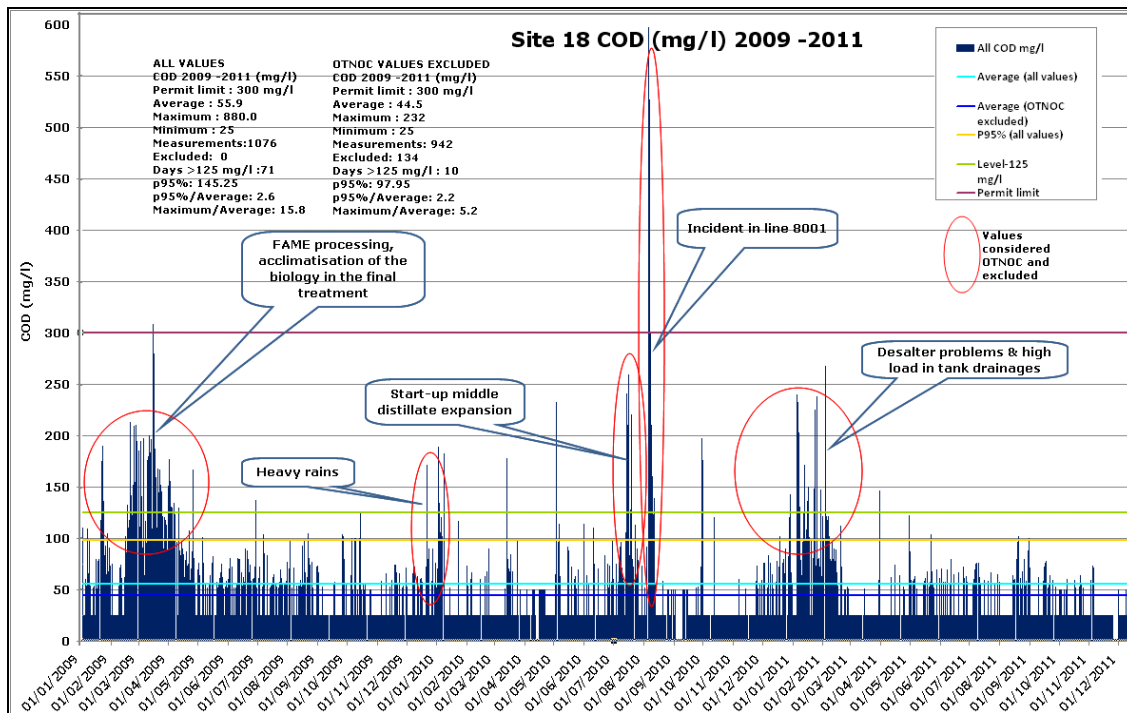


Figure 4.77: Example of a three-year data-set of COD concentrations (Site 18)

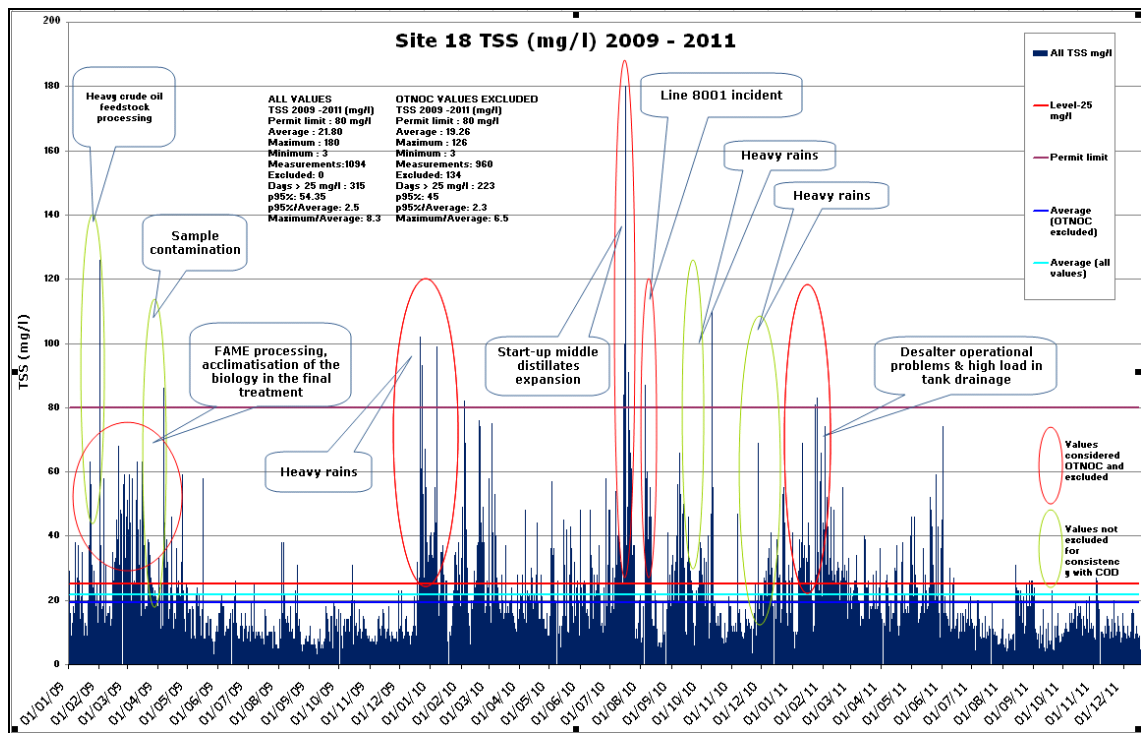


Figure 4.78: Example of a three-year data-set of TSS concentrations (Site 18)

Variance and achieved values for COD, TSS and TPH in the data-set

The following figures show, for each parameter (COD, TSS and TPH), on the first graph:

- the distribution of the annual average within the data-set;
- the minimum and maximum reported values;
- the outliers and the reasons for considering them as such.

For each parameter, the second associated graph shows the ordered values and the variability of the P95/AA ratio.

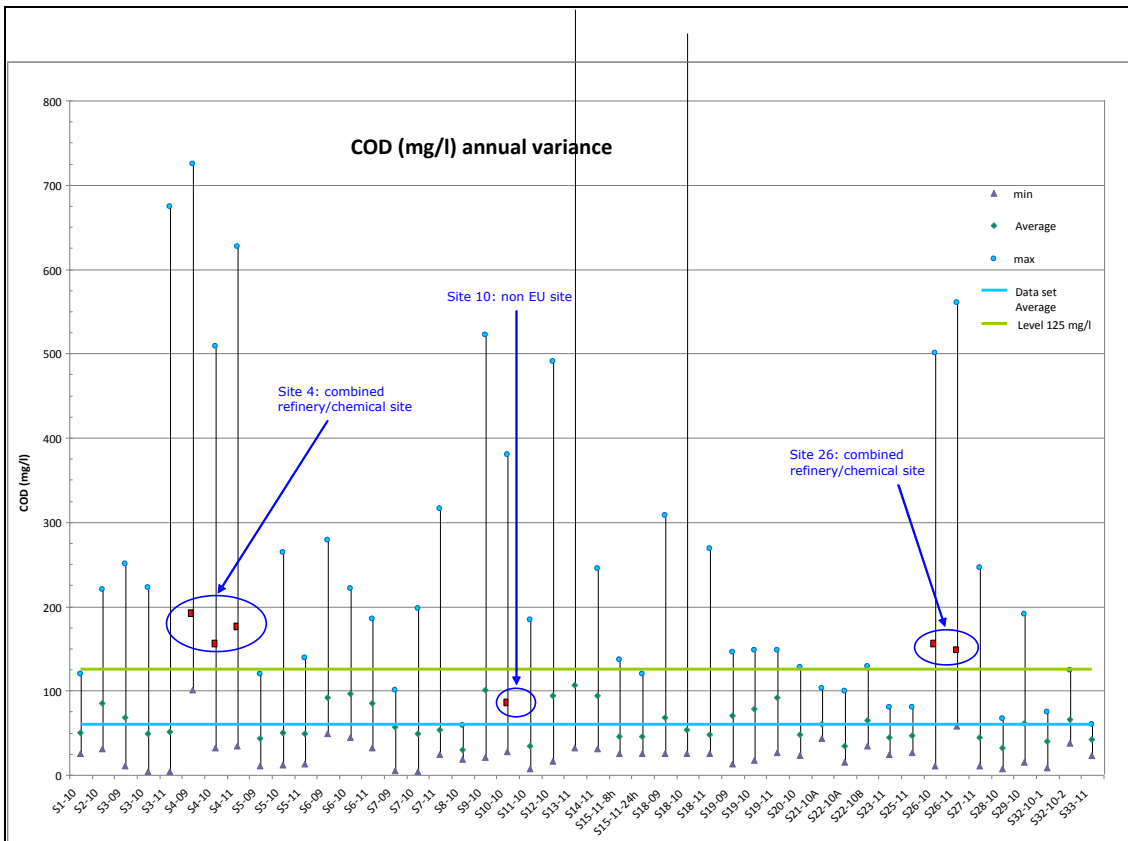


Figure 4.79: Annual variance for COD concentrations

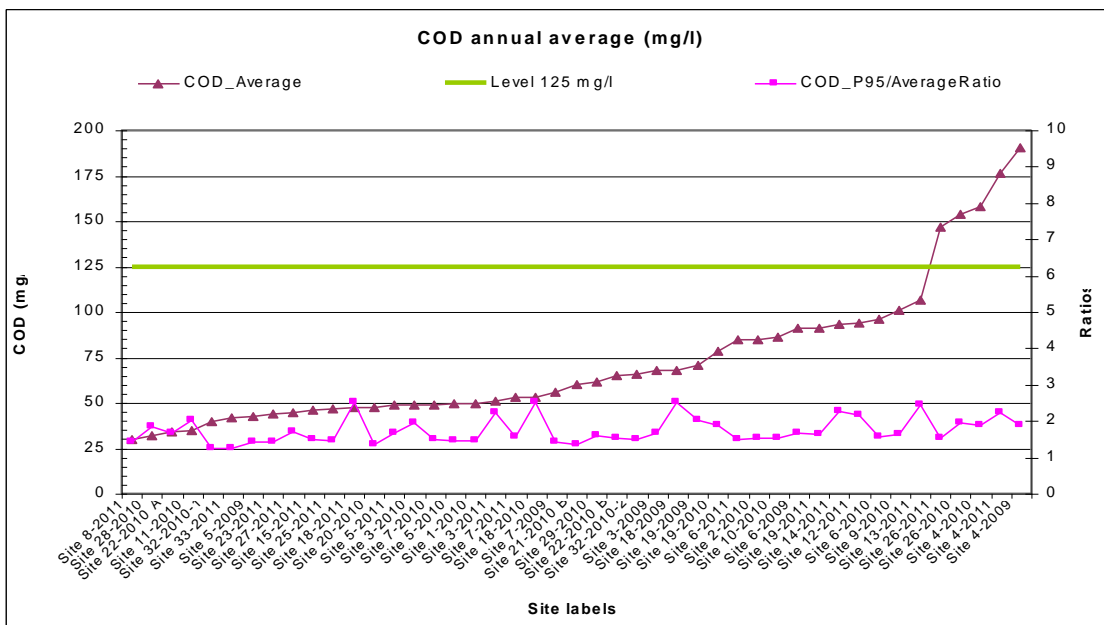


Figure 4.80: Achieved annual values and daily variations of COD concentrations

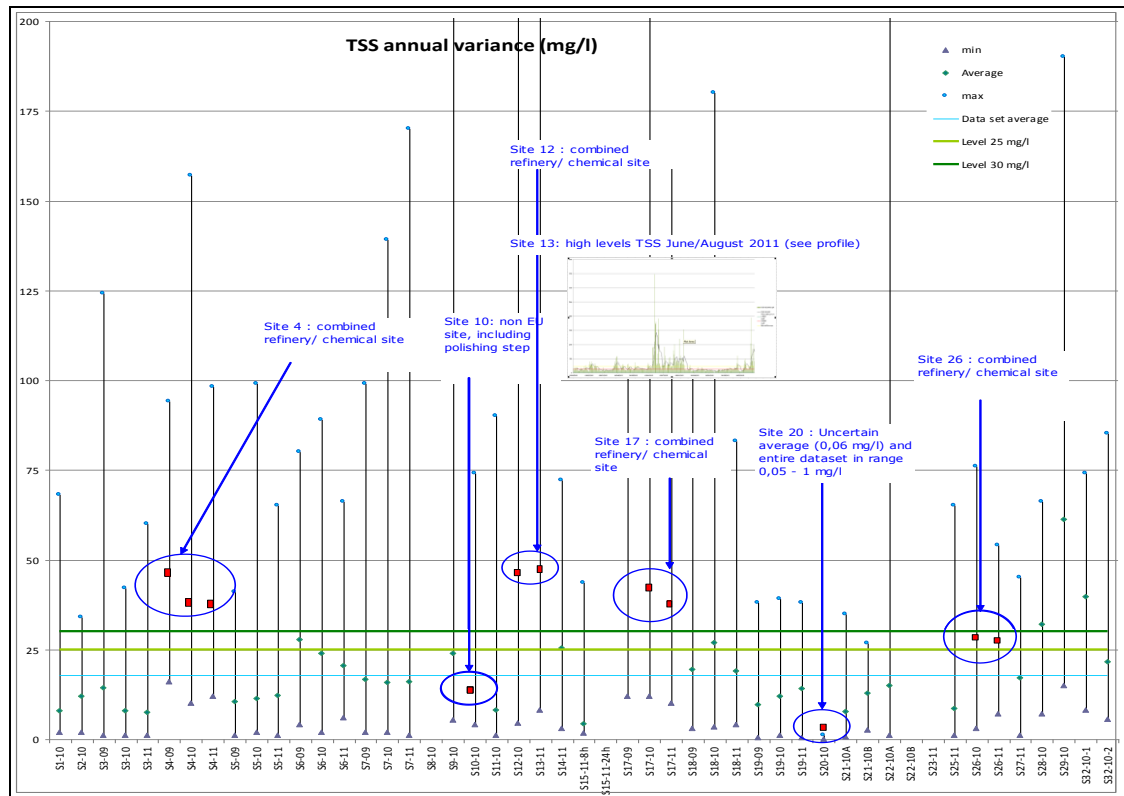


Figure 4.81: Annual variance of TSS concentrations

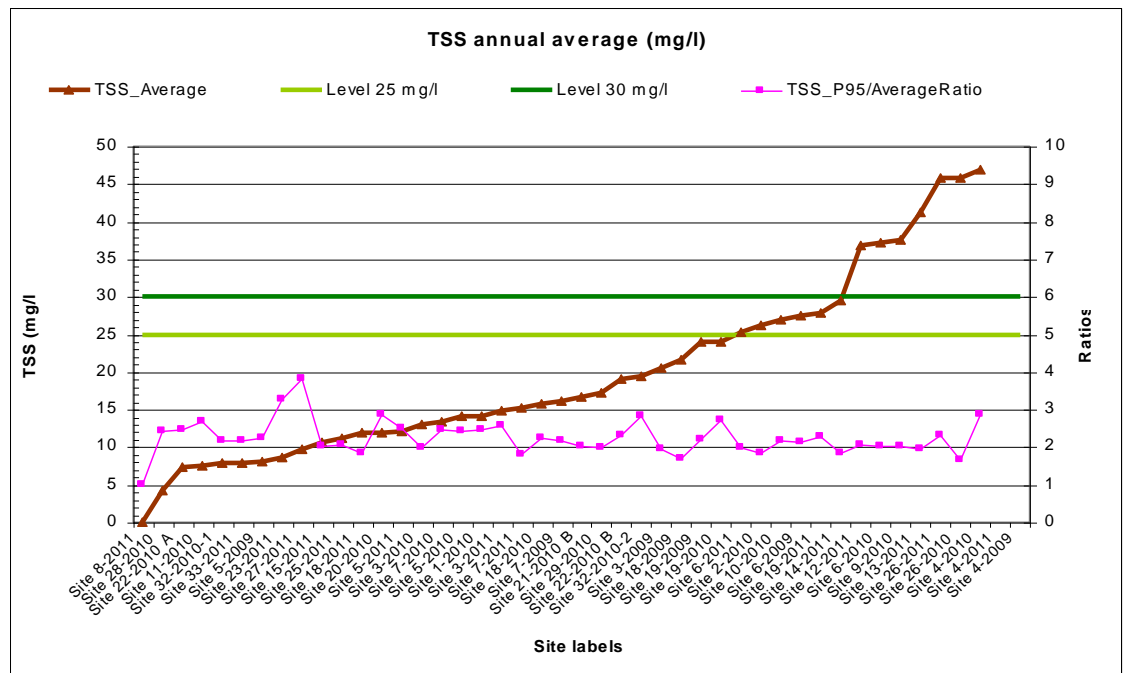


Figure 4.82: Achieved annual values and daily variations of TSS concentrations

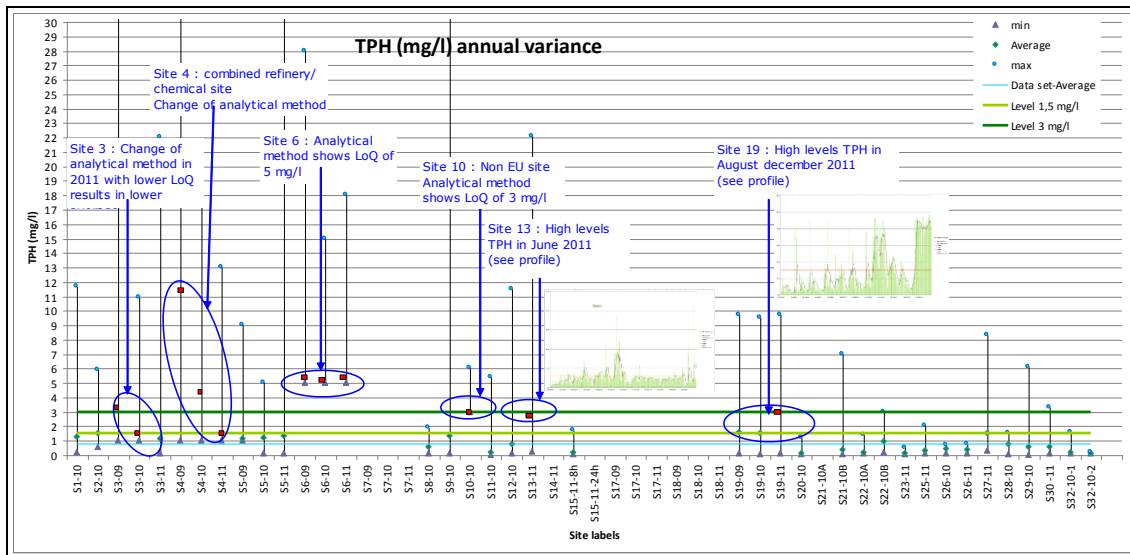


Figure 4.83: Annual variance of TPH concentrations

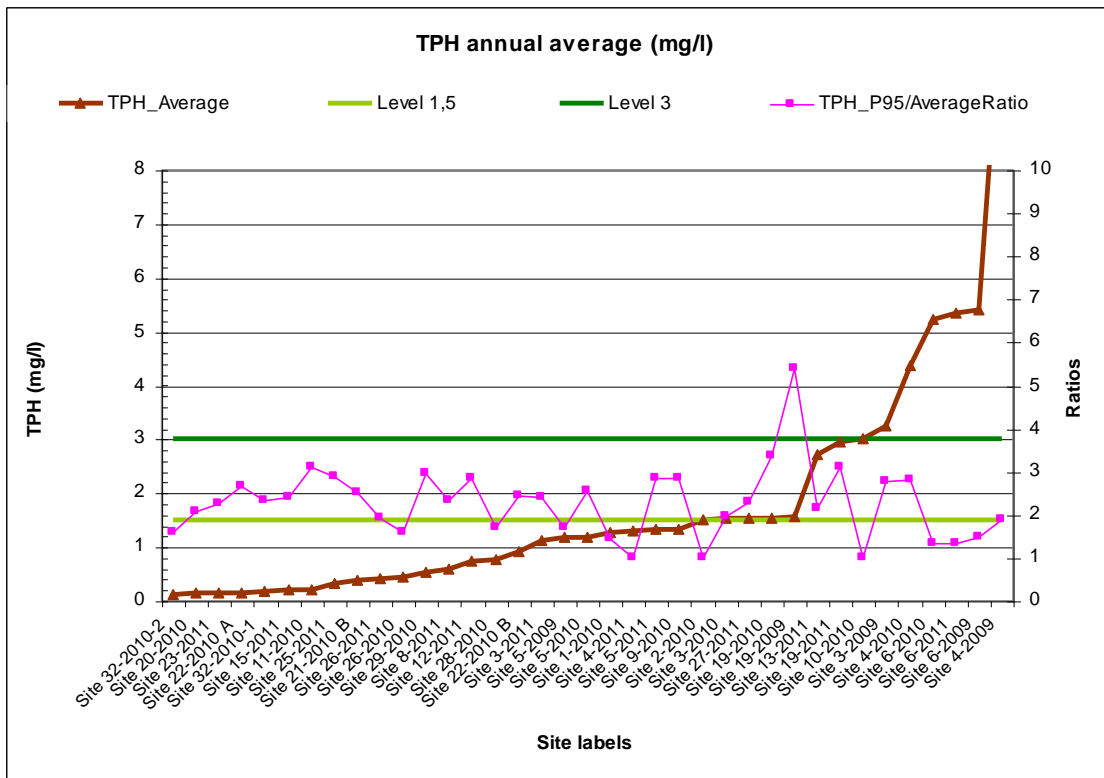


Figure 4.84: Achieved annual values and daily variations of TPH concentrations

Applicability

The WWTP system as described previously is applicable to all refineries to treat the discharge streams that require control and treatment. It may be advisable to install an observation basin between the final treatment step and the discharge to prevent any waste water that is not treated adequately from being directly discharged. In this case, the collected water can be re-routed for additional treatment. Such basins do require sufficient additional space to be available.

Reference literature

[77, REF TWG 2010 2010], [121, CONCAWE 2012], [122, CONCAWE 2010], [255, CONCAWE 2012]

4.24.7 Reduction of odours

4.24.7.1 Reduction of odours from WWTP

Description

For various steps of WWT, emissions to air of VOCs (including benzene) and odorous components (hydrogen sulphides and mercaptans) are directly related to the surface area of the open separation and collection compartments. The release of dissolved gases in the dissolved gas flotation (DGF) unit increases the effective water area exchanging with air and produces a continuous gas flow through the water column into the gas space above the liquid surface. The substances volatilised by diffusion into the gas bubbles and above the water column are then subject to ambient air convection. The generation of VOCs and odours can be further reduced by covering these units with closed and tightly sealed covers. However, due to eventual fluctuations of the internal pressure, such covers cannot be 100 % tight and have to be mechanically protected by an atmospheric vent. To be considered acceptable in order to protect covers together with minimising convective losses, the usual dimensions of such vents are around 0.90 m minimum height and 10.2 cm maximum diameter. An additional pressure relief/vacuum breaker valve can also be installed, in order to accommodate an exceptional gas exchange rate beyond the vent capacity.

Cover vents can be collected and treated with an appropriate off-gas treatment system (e.g. biofilter, activated carbon absorber, incinerator, thermal oxidiser - see Section 4.23.6.3) or can be reinjected into the aeration basin.

Achieved environmental benefits

VOC emissions from oil separators can be reduced to 3 g/m³ by covering the CPI and API.

The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [167, VDI 2000]:

- 20 g/m² per hour for open oil separator,
- 2 g/m² per hour for covered oil separator.

Cross-media effects

When separators are covered, the flammability/explosion limits and the toxicity concentration thresholds for some gaseous sulphur compounds may easily be reached. Consequently, occupational safety and environmental protection should be carefully considered at equipment design stage, and appropriate procedures should be set up for ensuring safe operating conditions. Safety should be addressed in the case of a fixed roof tank at any step of the WWT.

Applicability

Significant modifications may be needed before accepting a cover. Retrofitting to existing units may be complicated depending on the structural design, the type of mechanical float skimmers and solid scrapper systems used, as well as the position of electrical drivers.

Economics

For covering the first step separator units, the investment for the installation of two 200 m³ floating slab covers is about EUR 75 000 and the total annual operating costs about EUR 42 800 per year.

Table 4.133: VOC controls in oily water operations (installed and retrofitted)

| Emission Source | Oily water sewers/sumps/separations and drainage operations | | | |
|------------------------|---|--|-----------------------------------|------------------------------|
| | Automatic drainage facilities | Fixed/floating covers on APIs/sump | Incineration | 'Dry' oil collection systems |
| Control technique | Automatic drainage facilities | Fixed/floating covers on APIs/sump | Incineration | 'Dry' oil collection systems |
| Efficiency | 80 % | 80 – 90 % | 98 % | 90 % |
| Investment costs | EUR 0.002 – 0.03 million/tank ⁽¹⁾ | EUR 0.001 million/m ² ⁽¹⁾ | EUR 1 million ⁽¹⁾ | NA |
| Operating costs | Small | Moderate | EUR 0.1 million/yr ⁽¹⁾ | NA |
| Other impacts/comments | May not be suitable for all tank stocks | Limitation on access to APIs. Fixed covers may require purging systems | Assumes API is covered | NA |

⁽¹⁾ Source: Industry propriety information.

A floating cover (assuming an 800 m³/h process capacity of oily water, with VOC emissions up to 1 000 t/yr) will result in a 90 % VOC recovery efficiency for the following costs:

- investment costs: EUR 0.6 million;
- operating costs: EUR 0.03 million per year.

Example plants

Separators have been progressively covered in a growing number of European refineries.

4.24.7.2 Reduction of odours from water buffer tanks

Description

Water buffer tanks are used upstream and/or downstream of API/CPI/PPI separation systems to receive variable rate transfers of waste water containing insoluble floating oils, insoluble suspended oils and solids, and soluble substances. This section also includes process area storm water surge tanks.

As for any other treatment step, the generation of odours from open-top water buffer tanks will be directly related to the surface area of oil and water that will come into contact with air. Substances will be volatilised by diffusion into the air and be subjected to the convective forces of airflow. The generation of odours can be reduced by maintaining the smallest possible surface area of oil and water in contact with air. For such a purpose, the tank should be routinely checked and maintained free of oil by the operator, and the following actions can be taken.

- Operate the water buffer tank with a fixed roof equipped with a pressure relief/vacuum breaker valve to prevent convective losses when the tank level is static.
- Use an internal floating roof or an external floating roof equipped with at least a primary seal or, more efficiently, a primary and secondary seal between the floating roof and the tank shell, for further reducing the diffusive and convective losses.
- Instead of gravity draining to an open collection system, install an internal oil skimming system to extract oil from the tank through closed piping using a pump station or vacuum truck to minimise the possible loss of volatile substances. For safety reasons, in the case of using a vacuum truck, special care should be paid towards the flash point or H₂S concentrations in the liquid phase. The addition of carbonate neutraliser on the vapour phase of the truck can be considered.

Achieved environmental benefits

By using a fixed roof tank or a floating roof tank, the emission of VOCs and other odorous compounds can be reduced by 80 – 90 % compared to an open system. This ratio can be even

higher and reaches 99 – >99.9 % if vented emissions from the fixed roof tank are collected and routed to an appropriate off-gas treatment system (e.g. biofilter, activated carbon absorber, incinerator, thermal oxidiser - see Section 4.23.6.3).

Cross-media effects

Safety should be addressed in the case of a fixed roof tank (the same as for a DAF or a CPI unit).

Applicability

All new installations can be originally constructed with dual-sealing floating roofs or other systems with equivalent efficiency. Many existing water buffer tanks can be retrofitted with floating roofs, and existing floating roof tanks originally designed for crude or fuel storage can also be reused as water buffer tanks.

Economics

No data received for revamping and reuse of existing crude tanks as water buffer tanks.

Driving force for implementation

To reduce VOC emissions and odour pollution.

Example plants

Several examples in Europe.

Reference literature

[48, TOTAL 2010]

4.25 Waste management

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for waste generated by oil and gas refining. European legislation for waste is fully applicable to the refinery sector and especially the waste hierarchy which is described in Directive 2008/98/EC as a priority order in waste prevention and management, namely:

- prevention;
- preparing for reuse;
- recycling;
- other recovery, e.g. energy recovery;
- disposal.

For a given technique, available data on the way it can be applied and the results it enables to be achieved for particular processes or units have been given in the related sections. The information provided here aims at completing this information on the broader aspects, in particular environmental benefits, cross-media effects, operational data, and applicability issues which will not be repeated in other sections.

Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash. Other waste fractions are waste from flue-gas desulphurisation, fly ash, bottom ash, spent activated carbon, filter dust, inorganic salts as ammonium sulphate and lime from water pretreatment, oil-contaminated soil, bitumen, sweepings, spent acid and caustic solutions, and chemicals, among others. The treatment of these wastes includes incineration, land treating off site, landfilling on site, landfilling off site, chemical fixation, neutralisation, and other treatment methods.

4.25.1 Establishment of a waste management programme

Description

The establishment of an Environmental Management System (Section 4.15.1) contains elements to prevent waste generation. Some techniques that may be included are:

- implementation of a sludge master plan with the aim to reduce the sludge generated;
- provide enclosed sampling loops;
- cleaning and assembly preferably in specially constructed and dedicated areas;
- providing dedicated drainage systems;
- correct conditioning of a catalyst during a run, to extend catalytic life;
- control of sodium content in visbreaker feedstock, to reduce coke formation;
- process optimisation, to reduce off-specification products and hence recycling;
- recycling caustic sufficiently, to ensure it is completely spent;
- sorting waste mixes, e.g. concrete and scrap metal, as a cost-effective option (cheaper disposal routes for some components) and to eliminate the risk of unwanted components;
- asbestos lagging: special equipment for compaction and packing;
- where still relevant, apply permanganate treatment to eliminate traces of tetraethyl lead and tetramethyl lead (TEL/TML) in sludges;
- for oiled solids (soil): de-oiling in an oil extractor, neutralisation: mixing polymerisation catalyst (H_3PO_4) with lime;
- applying process treatment by steaming, flushing or regeneration prior to disposal: clay and sand filters; catalysts;

Additionally:

- Solids released to the waste water sewer system can account for a large portion of a refinery's oily sludges. Solids entering the sewer system (primarily soil particles) become coated with oil and are deposited as oily sludges in the API oil/water separator. Because a typical sludge has a solids content of 5 to 30 % w/w, preventing one kg of solids from entering the sewer system can eliminate 3 – 20 kg of oily sludge. The Amoco/US EPA study estimated that, at the Yorktown facility, 1 000 tonnes of solids per year enter the refinery sewer system. Methods used to control solids include: using a street sweeper on paved areas, paving unpaved areas, planting ground cover on unpaved areas, relining sewers, cleaning solids from ditches and catch basins, and reducing heat exchanger bundle cleaning solids by using antifoulants in cooling water.
- A significant portion of refinery waste arises from oily sludges found in combined process/storm sewers. When possible, segregation of the relatively clean rainwater runoff from the process streams can reduce the quantity of oily sludges generated. Furthermore, there is a much higher potential for the recovery of oil from smaller, more concentrated process streams.

Achieved environmental benefits

The aim of a waste management programme is to prevent the generation of waste and to reduce its final disposal.

Reference literature

[177, WRA 1999], [166, CONCAWE 1999], [228, TWG 2000].

4.25.2 Sludge management and treatment

Description

Sludges are defined as semi-liquid residue from industrial processes and waste water treatment. In refineries, a number of different types of sludges are generated at the following sources: crude and product tanks (bottoms), API separation units, flocculation and flotation units, and DAF units. Biological sludges represent a significant category of sludges in terms of oil content and dewaterability. Landfilling and land farming of sludges are severely restricted.

Pretreatment and treatment of sludge

The purpose of sludge treatment by dewatering, drying and/or incineration is to reduce the volume and the residual hydrocarbon content, in order to save the subsequent processing or disposal costs. The principle of mechanical dewatering by decanters is based on centrifugal forces and on the density difference between water, oil and solids. The principle of the thermal treatment steps is based on a combination of evaporation by indirect heating and/or the destruction of the organic constituents by thermal oxidation (incineration).

Decanter centrifuges are the most widely used for dewatering biosludges. Steam dryers are almost exclusively applied for biosludge and often as a pretreatment step for incineration.

Decanter centrifuges are widely used in sludge dewatering and de-oiling applications throughout the (refining) industry, either as fixed facilities or as a mobile service rendered by contractors. Dewatered biological and oily sludges can be further processed using drying and/or incineration techniques resulting in virtually oil-free residues for which useful applications are available.

Oily sludge dewatering is only applied at refineries that dispose of sludge cakes outside their premises in order to reduce the volume and associated disposal cost. Disposal to cement kilns, coal-fired power plants, dedicated sludge incinerators, municipal and hazardous waste incinerators are all used. Drying is hardly employed by refineries due to safety risks. De-oiling/dewatering of sludges gives a small volume of solid, low solvent waste, (centrifuging or

filtration). An option for refineries with cokers is to reuse oily sludges in the coking process, as already mentioned in Section 4.7.5.

Figure 4.85 shows a simplified process flow diagram of a decanter combined with a fluidised bed incinerator (FBI) that is considered BAT for sludge incineration in the WI BREF [81, COM 2006]. The feeding of sludge cake into the sand bed of the FBI can be accomplished with a positive displacement pump.

It should be mentioned that the emissions of SO₂, NO_x, CO, organic compounds, PAH and heavy metals generated by these systems should be properly controlled by suitable abatement techniques as addressed in the WI BREF.

In addition, other techniques for the management of sludges (including biological treatment) are described in the Waste Treatment BREF 2006 [87, COM 2006].

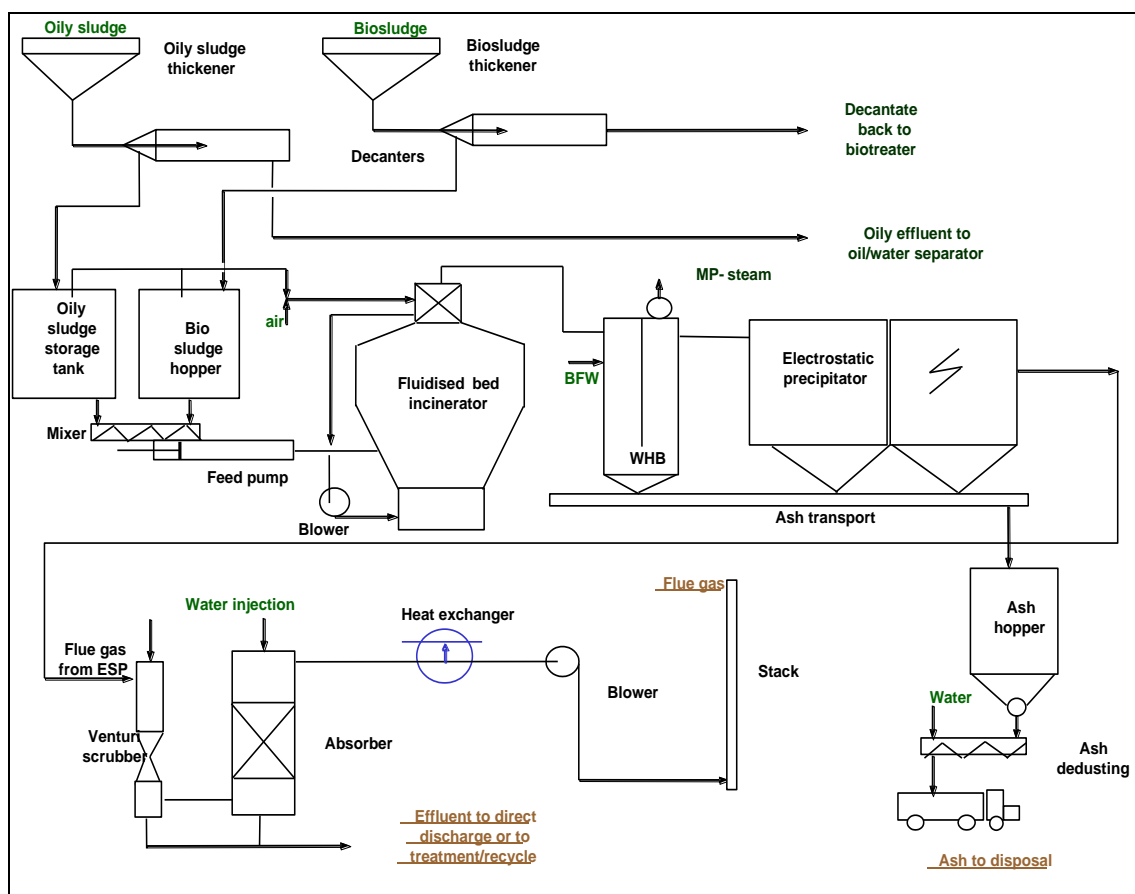


Figure 4.85: Simplified process flow diagram of sludge handling and incineration

Achieved environmental benefits

Generation of sludges can be reduced to values between 0.1 and 0.5 kg per tonne of feedstock processed within the refinery.

Cross-media effects

The cross media effects of sludge incineration are addressed in the WI BREF.

Operational data

Safety issues are associated with start-up and (planned or emergency) shutdown, for which a flame control interlock and a nitrogen purging system is required. Anaerobic and pyrophoric sludges (tank bottoms) can cause safety problems during storage and drying. The energy

requirements of sludge drying and incineration depend strongly on the sludge cake characteristics (water and residual oil contents). Energy integration with the FBI is twofold: air preheating of the primary fluidisation air is standard, and steam generation can be economically accomplished with systems able to generate more than 8 tonnes of MP steam/hour. An intrinsic disadvantage of the FBI is the relatively large excess of air utilised in order to keep the bed fluidised.

Applicability

Reuse of oily sludges in the coking process is dependent on the availability of this unit and the specifications of the final product. Dewatering units are fully applicable and are mainly used for waste minimisation before waste incineration. A fluidised bed incinerator (FBI) is a proven technology already fully applicable in the waste treatment industry.

Operational data and economics

For a FBI with a capacity of 4 t/h sludge cake (20 % dry solids), a footprint of about 50x100 m is required including tankage and complete flue-gas and ash handling. The installation is normally 12 – 15 m high (tanks, incinerator, WHB, ESP, ash hopper) and the stack height is usually at least 40 m, depending on ancillary installations. The system described above would be suitable for a large 20 Mt/yr refinery and requires a capital investment of about EUR 37.5 million (including installation). The operational costs could amount to EUR 500–700/tonne dry solids. If large-scale domestic sludge incinerators are available, which are authorised to take industrial sludges, the installation of a dedicated sludge incineration system is not economically justifiable.

A combination of decanters with an advanced drying system for oily sludge occupies only 10 – 15 % of the space indicated above, and would involve a capital investment of EUR 5 million, since expensive flue-gas treatment is avoided.

Driving force for implementation

Oil recovery. Operating cost reduction. Waste legislation.

Example plants

Decanter centrifuges are reliable, advanced and proven techniques with minimum emissions. At refinery locations, permanent decanter centrifuges have for example been installed at refineries in Godorf, Gothenburg and Stanlow. A few times per year, contractors are hired either for on-site sludge processing or for collection and off-site processing (decanting, drying, incineration in cement kilns, power plants or in industrial/domestic waste or dedicated sludge incinerators).

Sludge incineration plants using the fluidised bed system are considered state-of-the-art but require advanced design and process control. At several refineries, such as Mobil, Wilhelmshafen, Shell Pernis and Godorf, Esso Botlek, these systems were already built in the 1970s. Some of them have been dismantled due to the current availability of more economic options compared with the necessary investment and operation of additional flue-gas cleaning equipment for today's operation. For oily sludges, mixing with other wastes and use as secondary fuel in cement kilns and/or power plants is an attractive disposal route if these plants use appropriate abatement techniques. International sludge contractors employ either mobile decanter and drying systems for oil recovery (Impex, EPMS, Soil Recovery A/S) or fixed oily sludge treatment systems (ATM).

4.25.3 Spent solid catalyst management

The techniques used for the recovery of metals from secondary materials, such as the catalysts used in the oil and gas refining industry, are described in the NFM BREF [83, COM 2001].

The use of catalytic processes in refineries has increased significantly. This increase is mainly due to the introduction of catalytic residue conversion processes, such as heavy oil residue

cracking, hydrocracking and residue hydroconversion, hydrodemetallisation and hydrofinishing and also hydrogen production. Since 1980, a significant expansion of the hydrotreating and hydrodesulphurisation capacity has taken place, as well as of sulphur recovery units and associated tail gas treatment, whose processes also utilise catalysts. Traditional catalytic processes such as fluid catalytic cracking, catalytic reforming and isomerisation are also generators of spent catalysts.

The purpose of spent catalyst management is to minimise environmental and health impacts. To achieve this goal, spent catalysts are carefully handled, safely removed, carefully packed and sent for reactivation or metal reclamation. When the finally spent catalyst is no longer regenerable, it is sent to metal reclamation or to other waste treatments. Metal recovery aims at the conversion of spent catalysts into useful products, which can be recycled and reused with minimum impact on the environment.

The principle of spent catalyst management is a scheduled, strictly regulated and safe handling of the materials involved, usually executed by specialised contractors during plant turnarounds. Arrangements with the supplier of fresh catalyst can sometimes be made for them to take back the spent catalyst.

The regeneration of hydroprocessing catalysts is usually possible three or four times. The finally spent catalysts are almost exclusively reworked by third parties into commercial metal oxides or metal salt solutions. Although a regeneration process has been developed for spent FCC catalysts, this process is hardly used due to the availability of cheaper alternatives. The catalyst carrier (alumina and/or silica) can sometimes be converted into products or otherwise disposed of. Some refineries store spent catalysts at the refinery site in appropriate environmental conditions with the permission of the authorities. Spent catalysts are distinguished by type, process, composition and recyclability. A summary is given in Table 3.94 and below.

- Co/Mo catalysts from hydrodesulphurisation, hydrocracking, hydrotreating. Extensive regeneration and reclamation options are available.
- Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. Regeneration and reclamation capacity is available.
- Ni/W catalysts are used in lube oil hydrofinishing. This category experiences disposal limitations in view of the high tungsten content (24 % w/w).
- FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries. Outlets in road building are becoming available.
- Reformer and Isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved.
- Hydrodemetallisation catalysts typically have high vanadium contents (10 – 20 %) and are currently alumina-based (used to be silica). Direct disposal to the steel industry is possibly the most cost-effective option.
- Zn-containing beds from H₂ plants are typically recycled to the Zn industry where ZnS ores are processed. Amounts are some 50 t/yr.

The applied regeneration processes are based on pyrometallurgical techniques (roasting, calcination, smelting, sintering and reduction furnaces) for the thermal destruction of the inorganic matrix and on hydrometallurgical methods (aqueous/acid extraction, crystallisation, precipitation, separation and drying) for the recovery/purification of metal salts, either in dry form or as liquid metal concentrates.

The reclamation plants (more information can be found in the NFM BREF [83, COM 2001]) are typically operated in batch mode and contain many different unit operations. From the total spent catalysts, only some 5 % pure products are produced. The remainder is either ferro-alloy feed or ceramic raw material. The plant usually processes relatively small batches. Spent

hydroprocessing catalysts can vary considerably in composition. Hence the plants have limited process automation.

4.25.3.1 Control and reuse of the catalyst fines

Description

Significant quantities of catalyst fines are often present around the catalyst hoppers, reactors and regeneration vessels of the FCC unit, as well as those collected by the abatement techniques mentioned above. The fines can be collected and recycled before being washed to the sewers or migrating off site via the wind. These techniques may be considered housekeeping measures, and are thus included in Section 4.15. Some techniques to consider are:

- dry sweeping the catalyst fines and sending the solids to be recycled or disposed of as non-hazardous waste;
- using vacuum ducts in dusty areas (and vacuum hoses for manual collection), which run to a small baghouse for collection;
- reusing the fines (cement production);
- returning FCC spent catalysts back to the manufacturer.

Achieved environmental benefits

Reduced emission of particulates.

Cross-media effects

None of note.

Operational data

No data available.

Applicability

Fully applicable especially during catalyst loading/unloading processes.

Economics

No data available.

Driving force for implementation

Reduction of soil contamination by particulates.

Example plants

Techniques already in use in US refineries.

Reference literature

[156, MCG 1991].

4.25.3.2 Removal of catalyst from slurry decant oil

Description

Three types of techniques are applied to improve the separation of catalysts from the slurry decant oil used in catalytic crackers. One system incorporates high-voltage electric fields to polarise and capture catalyst particles from decant oil; here, catalyst fines suspended in the separator underflow are recycled back to the reactor. In another system, the amount of catalyst fines reaching the decant oil can be minimised by installing high-efficiency cyclones in the reactor, to shift the catalyst fines losses of the decant oil to the regenerator, where they can be collected by any particulate abatement technique. A third method is to use a mechanical filter with backwash.

Achieved environmental benefits

Decant oil sludge from a FCC can contain significant concentrations of catalyst fines. These fines often do not allow use of the decant oil as a feedstock and require treatment which generates an oily catalyst sludge. Catalysts in the decant oil can be minimised by using a decant oil catalyst removal system.

Cross-media effects

These techniques have their own energy consumption.

Operational data

No data available.

Economics

No data available.

Applicability

Hydrocyclones are applied in many FCC units.

Driving force for implementation

Reduction of consumption of catalyst and reduction of the decant oil sludge.

Example plants

Hydrocyclones, for removal of catalyst fines, are successfully applied in many FCCs.

Reference literature

[228, TWG 2000]

4.25.4 Recycling and reusing waste

Recycling and reuse of unintended by-products in different refinery processes or outside the refinery reduces the quantity of waste for disposal.

4.25.4.1 Treatment of heavy residues

Heavy residues generated by refineries are the heaviest fractions from the different units (distillation, conversion). These residues may be mixed with bitumen or other residues fractions if meeting the specifications of a product. They may not have application for products and are typically reused within the refinery where their calorific value can be exploited. Below is a list of treatments that may be applied to reduce the amount of these residues. All these techniques are already analysed in other sections but are put together here to help the reader to understand what refineries may do with their heavy residues.

Methods to increase the hydrogen content (hydrogenation):

- Catalytic hydrogenation (included within Section 4.13) such as Resid Fining, RCD UNIBON, Unicracking, HYVAHL-ASVAHL hydrotreatment, AUROBAN, H-Oil, LC-Fining, HYCON.
- Non-catalytic hydrogenation (included within Section 4.22) as Hydrovisbreaking, Dynacracking, Donor Solvent Visbreaking.

Methods to increase the C content:

- Catalytic cracking (included within Section 4.5) such as residue catalytic cracking (RCC), Heavy oil Cracking, VEBA combi cracking (VCC), Deep catalytic cracking (DCC).

- Non-catalytic cracking (included within Sections 4.7 and 4.22) as delayed coking, fluid coking, flexicoking, LR-Coking, deasphalting: DEMEX, Rose-Technology, visbreaking, thermal cracking, and partial oxidation.

4.25.4.2 Improve the recovery of oils from oily sludges

Because oily sludges make up a large portion of refinery solid wastes, any improvement in the recovery of oil from the sludges can significantly reduce the volume of waste. There are a number of technologies currently in use to mechanically separate oil, water and solids, including: belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll centrifuges, disc centrifuges, shakers, thermal dryers and centrifuge-dryer combinations.

4.25.4.3 Regenerate or eliminate filtration clay

Clay from refinery filters must periodically be replaced. Spent clay often contains significant amounts of entrained hydrocarbons and, therefore, must be designated as hazardous waste. Techniques that may be applied are:

- backwashing spent clay with water or steam to reduce the hydrocarbon content to levels so that it can be reused or handled as a non-hazardous waste;
- washing the clay with naphtha, drying it by steam heating and then feeding it to a burning kiln for regeneration;
- in some cases, clay filtration can be entirely replaced with hydrotreating (see Section 4.20.4).

4.25.4.4 Reprocessing off-specification products

It is customary in refineries to have dedicated tankage (or ‘slops’) for the collection of hydrocarbon streams/intermediate products that cannot be blended into final products for the market. These slops are generally reprocessed, often by injection into the crude oil feedstock to the crude distilling unit or to the coker. Often, segregation is practised between wet and dry slops (as a general rule the wet slop contains significant amounts of dissolved and emulsified water and is unsuitable for direct reprocessing – the dry slop is sufficiently dehydrated to be ready for reprocessing). The wet slops tank is equipped with facilities to separate (drain) water from oil (to prevent slugs of water from coming into the crude distiller). In some refineries, separate slops processing (distillation) facilities are installed [202, Dekkers 2000].

Streams from water treatment units (e.g. oil/water mixtures from interceptors) can be routed to the wet slops tank. Oil from sludge thickeners (centrifuges/decanter) can be routed to the slops tanks. The oil in sludges (e.g. from DAF units) can be recovered in this way also [202, Dekkers 2000].

4.25.4.5 Recycle/Reuse outside the installation

Some options to reduce the waste generation are to recycle or reuse them. Below are some examples of good environmental practices.

- Treat catalysts for metal recovery (reforming, desulphurisation) (see Section 4.20.2).
- Waste lubes: re-refining or reuse (see Section 4.25.4.6).
- Drums/containers: reconditioning.
- Spent caustic can be used: (see Section 4.20.2).
- Alkylation process: CaF_2 can be used:

- for HF production,
- as a fluxing agent (steel industry).
- Resale of polymerisation plant catalyst as a fertiliser (see Section 4.18.2).
- Sale of gypsum or sulphuric acid from flue-gas desulphurisation units.
- For dust: in the regenerative flue-gas desulphurisation process according to Wellman-Lord, NH_3 is injected to prevent the formation of SO_3 . Therefore up to 80 % of the ash consists of $(\text{NH}_4)_2\text{SO}_4$, which can be used as a fertiliser or as a basic material for NH_3 production [194, Winter 2000].
- Paper, wood, glass, scrap metal selective collection and recycling schemes and circuits which may be implemented at national or regional levels.
- Construction/demolition debris:
 - concrete to a crusher, for use in road building, etc.
 - asphalt scrapings reused, e.g. in road building.

It has to be mentioned that reuse of waste fractions/residues outside the company is only an option, but needs to comply with the requirements of the Waste Framework Directive (2008/98/EC), if these waste fractions meet certain criteria (such as concentration of pollutants in a fertiliser) and do not alter the original product characteristics (e.g. when using gypsum in the cement industry).

4.25.4.6 Reuse of waste lubes

Description

Waste lubes can be reused within the refinery as a fuel component or as feedstock for re-refining. Controlled incineration of waste lube oils is another alternative.

Achieved environmental benefits

Reduction of the amount of waste lubes produced within the refinery.

Cross-media effects

Waste lubricating oils may contain additives that need to be disposed of properly.

Applicability

Some applicability problems have been detected. For example, waste lubricating oil from garages may contain organic chlorides used as degreasers; in hydrotreaters they will be converted into HCl and can cause severe corrosion in this high-pressure unit filled with hydrogen. Only by application of well-controlled pretreatment techniques can the treated waste oil be upgraded to a fuel component. Such a pretreatment activity is normally not compatible with refinery operations and is carried out outside the refinery by specialised companies, which also collect the waste oils. The only exception to the use of waste lubes as a fuel component is for waste lube oil that is generated in the refinery itself and whose composition is beyond any doubt.

Driving force for implementation

To reduce the amount of waste lubes.

Reference literature

[202, Dekkers 2000].

4.25.4.7 Recycle lab samples

Lab samples can be recycled to the oil recovery system.

4.25.5 Biodegradation of wastes

This section contains methods for the biodegradation of refinery wastes that may be used specifically within refineries on site. This section does not contain methods for the remediation of contaminated soils. As was stated in the scope of this document, soil remediation techniques are considered outside the scope of this document.

Description

Many hazardous chemicals present in refinery waste can be converted by microbiological methods to harmless compounds such as water and carbon dioxide. In general, the microbiological degradation of contaminants in soil is very slow in nature, because process conditions for such degradation are seldom favourable. To accelerate degradation, a number of conditions have to be fulfilled.

Current techniques for biological decontamination are based on optimisation of the process conditions for microbiological degradation. The appropriate microorganisms for microbiological degradation may already be present in the waste to be treated or may have to be added. The latter is necessary if special microorganisms are required. These special microorganisms can be achieved by selection and adaptation.

Other techniques for bioremediation are described in the Waste Treatment BREF [87, EC 2006].

Operational data

The most important factors are the availability of temperature control, sufficient oxygen, nutrients, and the appropriate microorganisms. Also important are the concentration levels of the contaminants and the variation in concentration. The presence of toxic compounds can disturb the degradation process. Sometimes the presence of natural organic compounds has a positive influence on the biodegradation process.

In summary, the following conditions have to be met in order to optimise the degradation rate of a waste generated by a refinery:

- sufficient number of microorganisms of the right strains;
- non-toxic concentrations of contaminants or other compounds;
- adjustment of an accurate water content;
- presence of sufficient nutrients (mainly P and N in ratio 1:10);
- presence of sufficient oxygen for aerobic processes and a full depletion of oxygen for anaerobic processes;
- favourable temperature (20 – 30°C);
- pH 6 – 8;
- temperature control;
- measures have to be applied to prevent emissions into air by volatile contaminants or degradation products (by covering the area and by treating the exhaust air) and to prevent emissions into water and soil (by sealing the floor and reuse of excess water);
- sufficient availability of contaminants (preferably without high peak concentrations) to the microorganisms including good mixing of nutrients, waste, inerts (e.g. soil) and contaminants.

Reference literature

[87, COM 2006], [166, CONCAWE 1999].

4.25.6 Waste storage

Wastes awaiting disposal should be stored in an environmentally acceptable manner, as approved by the local control authority. Storage should not give rise to secondary environmental problems, such as odour or pollution of groundwater due to rainwater percolation or run-off from the site. Storage should be in closed vessels, containers or bags, on a site surrounded by a bund wall or toe wall, with drainage to a prepared system. Special precautions are of course required for pyrophoric materials to eliminate the risk of fires; they must be kept wet, sealed or blanketed with inert gas.

5 BEST AVAILABLE TECHNIQUES (BAT) CONCLUSIONS

SCOPE

These BAT conclusions cover certain industrial activities specified in Section 1.2 of Annex I to Directive 2010/75/EU, namely '1.2. Refining of mineral oil and gas'.

In particular, these BAT conclusions cover the following processes and activities:

| Activity | Subactivities or processes included in activity |
|--|---|
| Alkylation | All alkylation processes: hydrofluoric acid (HF), sulphuric acid (H ₂ SO ₄) and solid-acid |
| Base oil production | Deasphalting, aromatic extraction, wax processing and lubricant oil hydrofinishing |
| Bitumen production | All techniques from storage to final product additives |
| Catalytic cracking | All types of catalytic cracking units such as fluid catalytic cracking |
| Catalytic reforming | Continuous, cyclic and semi-regenerative catalytic reforming |
| Coking | Delayed and fluid coking processes. Coke calcination |
| Cooling | Cooling techniques applied in refineries |
| Desalting | Desalting of crude oil |
| Combustion units for energy production | Combustion units burning refinery fuels, excluding units using only conventional or commercial fuels |
| Etherification | Production of chemicals (e.g. alcohols and ethers such as MTBE, ETBE and TAME) used as motor fuels additives |
| Gas separation | Separation of light fractions of the crude oil e.g. refinery fuel gas (RFG), liquefied petroleum gas (LPG) |
| Hydrogen consuming processes | Hydrocracking, hydrorefining, hydrotreatments, hydroconversion, hydroprocessing and hydrogenation processes |
| Hydrogen production | Partial oxidation, steam reforming, gas heated reforming and hydrogen purification |
| Isomerisation | Isomerisation of hydrocarbon compounds C ₄ , C ₅ and C ₆ |
| Natural gas plants | Natural gas (NG) processing including liquefaction of NG |
| Polymerisation | Polymerisation, dimerisation and condensation |
| Primary distillation | Atmospheric and vacuum distillation |
| Product treatments | Sweetening and final product treatments |
| Storage and handling of refinery materials | Storage, blending, loading and unloading of refinery materials |
| Visbreaking and other thermal conversions | Thermal treatments such as visbreaking or thermal gas oil process |
| Waste gas treatment | Techniques to reduce or abate emissions to air |
| Waste water treatment | Techniques to treat waste water prior to release |
| Waste management | Techniques to prevent and reduce the generation of waste |

These BAT conclusions do not address the following activities or processes:

- the exploration and production of crude oil and natural gas;
- the transportation of crude oil and natural gas;
- the marketing and distribution of products.

Other reference documents which may be relevant for the activities covered by these BAT conclusions are the following:

| Reference document | Subject |
|--|--|
| Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW) | Waste water management and treatment techniques |
| Industrial Cooling Systems (ICS) | Cooling processes |
| Economics and Cross-media Effects (ECM) | Economics and cross-media effects of techniques |
| Emissions from Storage (EFS) | Storage, blending, loading and unloading of refinery materials |
| Energy Efficiency (ENE) | Energy efficiency and integrated refinery management |
| Large Combustion Plants (LCP) | Combustion of conventional and commercial fuels |
| Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (LVIC-AAF) | Steam reforming and hydrogen purification |
| Large Volume Organic Chemical Industry (LVOC) | Etherification process (MTBE, ETBE and TAME production) |
| Waste Incineration (WI) | Waste incineration |
| Waste Treatment (WT) | Waste treatment |
| General Principles of Monitoring (MON) | Monitoring of emissions to air and water |

GENERAL CONSIDERATIONS

The techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive. Other techniques may be used that ensure at least an equivalent level of environmental protection.

Unless otherwise stated, these BAT conclusions are generally applicable.

Averaging periods and reference conditions for emissions to air

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for emissions to air given in these BAT conclusions refer to concentrations, expressed as mass of emitted substance per volume of waste gas under the following standard conditions: dry gas, temperature of 273.15 K, pressure of 101.3 kPa.

| | |
|-----------------------------|---|
| For continuous measurements | BAT-AELs refer to monthly average values, which are the averages of all valid hourly average values measured over a period of one month |
| For periodic measurements | BAT-AELs refer to the average value of three spot samples of at least 30 minutes each |

For combustion, catalytic cracking processes, and waste gas sulphur recovery units, reference conditions for oxygen are shown in Table 5.1.

Table 5.1: Reference conditions for BAT-AELs concerning emissions to air

| Activities | Unit | Oxygen reference conditions |
|--|--------------------|-----------------------------|
| Combustion unit using liquid or gaseous fuels with the exception of gas turbines and engines | mg/Nm ³ | 3 % oxygen by volume |
| Combustion unit using solid fuels | mg/Nm ³ | 6 % oxygen by volume |
| Gas turbines (including combined cycle gas turbines – CCGT) and engines | mg/Nm ³ | 15 % oxygen by volume |
| Catalytic cracking process (regenerator) | mg/Nm ³ | 3 % oxygen by volume |
| Waste gas sulphur recovery unit ⁽¹⁾ | mg/Nm ³ | 3 % oxygen by volume |
| ⁽¹⁾ In case of applying BAT 58. | | |

Conversion of emissions concentration to reference oxygen level

The formula for calculating the emissions concentration at a reference oxygen level (see Table 5.1) is shown below.

$$E_R = \frac{21 - O_R}{21 - O_M} \times E_M$$

Where:

- E_R (mg/Nm³): emissions concentration corrected to the reference oxygen level O_R
 O_R (% v/v): reference oxygen level
 E_M (mg/Nm³): emissions concentration referred to the measured oxygen level O_M
 O_M (% v/v): measured oxygen level.

Averaging periods and reference conditions for emissions to water

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for emissions to water given in these BAT conclusions refer to values of concentration (mass of emitted substances per volume of water) expressed in mg/l.

Unless stated otherwise, the averaging periods associated with the BAT-AELs are defined as follows:

| | |
|------------------------|---|
| Daily average | Average over a sampling period of 24 hours taken as a flow-proportional composite sample or, provided that sufficient flow stability is demonstrated, from a time-proportional sample |
| Yearly/Monthly average | Average of all daily averages obtained within a year/month, weighted according to the daily flows |

DEFINITIONS

For the purpose of these BAT conclusions, the following definitions apply:

| Term used | Definition |
|--|---|
| Unit | A segment/subpart of the installation in which a specific processing operation is conducted |
| New unit | A unit first permitted on the site of the installation following the publication of these BAT conclusions or a complete replacement of a unit on the existing foundations of the installation following the publication of these BAT conclusions |
| Existing unit | A unit which is not a new unit |
| Process off-gas | The collected gas generated by a process which must be treated e.g. in an acid gas removal unit and a sulphur recovery unit (SRU) |
| Flue-gas | The exhaust gas exiting a unit after an oxidation step, generally combustion (e.g. regenerator, Claus unit) |
| Tail gas | Common name of the exhaust gas from an SRU (generally Claus process) |
| VOC | Volatile organic compounds as defined in Article 3(45) of Directive 2010/75/EU |
| NM VOC | VOC excluding methane |
| Diffuse VOC emission | Non-channelled VOC emissions that are not released via specific emission points such as stacks. They can result from 'area' sources (e.g. tanks) or 'point' sources (e.g. pipe flanges) |
| NO _x expressed as NO ₂ | The sum of nitrogen oxide (NO) and nitrogen dioxide (NO ₂) expressed as NO ₂ |
| SO _x expressed as SO ₂ | The sum of sulphur dioxide (SO ₂) and sulphur trioxide (SO ₃) expressed as SO ₂ |
| H ₂ S | Hydrogen sulphide. Carbonyl sulphide and mercaptan are not included |
| Hydrogen chloride expressed as HCl | All gaseous chlorides expressed as HCl |
| Hydrogen fluoride expressed as HF | All gaseous fluorides expressed as HF |
| FCC unit | Fluid catalytic cracking: a conversion process for upgrading heavy hydrocarbons, using heat and a catalyst to break larger hydrocarbon molecules into lighter molecules |
| SRU | Sulphur recovery unit. See definition in Section 5.20.3 |
| Refinery fuel | Solid, liquid or gaseous combustible material from the distillation and conversion steps of the refining of crude oil. Examples are refinery fuel gas (RFG), syngas and refinery oils, pet coke |
| RFG | Refinery fuel gas: off-gases from distillation or conversion units used as a fuel |
| Combustion unit | Unit burning refinery fuels alone or with other fuels for the production of energy at the refinery site, such as boilers (except CO boilers), furnaces, and gas turbines. |
| Continuous measurement | Measurement using an 'automated measuring system' (AMS) or a 'continuous emission monitoring system' (CEMS) permanently installed on site |
| Periodic measurement | Determination of a measurand at specified time intervals using manual or automated reference methods |
| Indirect monitoring of emissions to air | Estimation of the emissions concentration in the flue-gas of a pollutant obtained through an appropriate combination of measurements of surrogate parameters (such as O ₂ content, sulphur or nitrogen content in the feed/fuel), calculations and periodic stack measurements. The use of emission ratios based on S content in the fuel is one example of indirect monitoring. Another example of indirect monitoring is the use of PEMS |

| Term used | Definition |
|---|---|
| Predictive Emissions monitoring system (PEMS) | System to determine the emissions concentration of a pollutant based on its relationship with a number of characteristic continuously monitored process parameters (e.g. fuel-gas consumption, air/fuel ratio) and fuel or feed quality data (e.g. the sulphur content) of an emission source |
| Volatile liquid hydrocarbon compounds | Petroleum derivatives with a Reid vapour pressure (RVP) of more than 4 kPa, such as naphtha and aromatics |
| Recovery rate | Percentage of NMVOC recovered from the streams conveyed into a vapour recovery unit (VRU) |

5.1 General BAT conclusions for the refining of mineral oil and gas

The process-specific BAT conclusions included in Sections 5.2 to 5.19 apply in addition to the general BAT conclusions mentioned in this section.

5.1.1 Environmental management systems

BAT 1. In order to improve the overall environmental performance of plants for the refining of mineral oil and gas, BAT is to implement and adhere to an environmental management system (EMS) that incorporates all of the following features:

- i. commitment of the management, including senior management;
- ii. definition of an environmental policy that includes the continuous improvement for the installation by the management;
- iii. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
- iv. implementation of the procedures paying particular attention to:
 - (a) structure and responsibility
 - (b) training, awareness and competence
 - (c) communication
 - (d) employee involvement
 - (e) documentation
 - (f) efficient process control
 - (g) maintenance programmes
 - (h) emergency preparedness and response
 - (i) safeguarding compliance with environmental legislation.
- v. checking performance and taking corrective action, paying particular attention to:
 - (a) monitoring and measurement (see also the reference document on the General Principles of Monitoring)
 - (b) corrective and preventive action
 - (c) maintenance of records
 - (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
- vi. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
- vii. following the development of cleaner technologies;
- viii. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
- ix. application of sectoral benchmarking on a regular basis.

Applicability

The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

5.1.2 Energy efficiency

BAT 2. In order to use energy efficiently, BAT is to use an appropriate combination of the techniques given below:

| Technique | Description |
|--|--|
| i. Design techniques | |
| a. Pinch analysis | Methodology based on a systematic calculation of thermodynamic targets for minimising energy consumption of processes. Used as a tool for the evaluation of total systems designs |
| b. Heat integration | Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled |
| c. Heat and power recovery | Use of energy recovery devices e.g.: <ul style="list-style-type: none"> • waste heat boilers • expanders/power recovery in the FCC unit • use of waste heat in district heating |
| ii. Process control and maintenance techniques | |
| a. Process optimisation | Automated controlled combustion in order to lower the fuel consumption per tonne of feed processed, often combined with heat integration for improving furnace efficiency |
| b. Management and reduction of steam consumption | Systematic mapping of drain valve systems in order to reduce steam consumption and optimise its use |
| c. Use of energy benchmark | Participation in ranking and benchmarking activities in order to achieve continuous improvement by learning from best practice |
| iii. Energy-efficient production techniques | |
| a. Use of combined heat and power | System designed for the co-production (or the cogeneration) of heat (e.g. steam) and electric power from the same fuel |
| b. Integrated gasification combined cycle (IGCC) | Technique whose purpose is to produce steam, hydrogen (optional) and electric power from a variety of fuel types (e.g. heavy fuel oil or coke) with a high conversion efficiency |

5.1.3 Solid materials storage and handling

BAT 3. In order to prevent or, where that is not practicable, to reduce dust emissions from the storage and handling of dusty materials, BAT is to use one or a combination of the techniques given below:

- i. store bulk powder materials in enclosed silos equipped with a dust abatement system (e.g. fabric filter);
- ii. store fine materials in enclosed containers or sealed bags;
- iii. keep stockpiles of coarse dusty material wetted, stabilise the surface with crusting agents, or store under cover in stockpiles;
- iv. use road cleaning vehicles.

5.1.4 Monitoring of emissions to air and key process parameters

BAT 4. BAT is to monitor emissions to air by using the monitoring techniques with at least the minimum frequency given below and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

| Description | Process unit | Minimum frequency | Monitoring technique |
|--|---|--|--|
| i. SO _x , NO _x , and dust emissions | Catalytic cracking | Continuous ⁽¹⁾ ⁽²⁾ | Direct measurement |
| | Combustion units ≥ 100 MW ⁽³⁾ and calcining units | Continuous ⁽¹⁾ ⁽²⁾ | Direct measurement ⁽⁴⁾ |
| | Combustion units of 50 to 100 MW ⁽³⁾ | Continuous ⁽¹⁾ ⁽²⁾ | Direct measurement or indirect monitoring |
| | Combustion units <50 MW ⁽³⁾ | Once a year and after significant fuel changes ⁽⁵⁾ | Direct measurement or indirect monitoring |
| | Sulphur recovery units (SRU) | Continuous for SO ₂ only ⁽²⁾ | Direct measurement or indirect monitoring ⁽⁶⁾ |
| ii. NH ₃ emissions | All units equipped with SCR or SNCR | Continuous | Direct measurement |
| iii. CO emissions | Catalytic cracking and combustion units ≥ 100 MW ⁽³⁾ | Continuous | Direct measurement |
| | Other combustion units | Once every 6 months ⁽⁵⁾ | Direct measurement |
| iv. Metals emissions: Nickel (Ni), Antimony (Sb) ⁽⁷⁾ , Vanadium (V) | Catalytic cracking | Once every 6 months and after significant changes to the unit ⁽⁵⁾ | Direct measurement or analysis based on metals content in the catalyst fines and in the fuel |
| | Combustion units ⁽⁸⁾ | | |
| v. Polychlorinated dibenzodioxins/furans (PCDD/F) emissions | Catalytic reformer | Once a year or once a regeneration, whichever is longer | Direct measurement |

⁽¹⁾ Continuous measurement of SO₂ emissions may be replaced by calculations based on measurements of the sulphur content of the fuel or the feed; where it can be demonstrated that this leads to an equivalent level of accuracy.

⁽²⁾ Regarding SO_x, only SO₂ is continuously measured, while SO₃ is only periodically measured (e.g. during calibration of the SO₂ monitoring system).

⁽³⁾ Refers to the total rated thermal input of all combustion units connected to the stack where emissions occur.

⁽⁴⁾ Or indirect monitoring of SO_x.

⁽⁵⁾ Monitoring frequencies may be adapted if, after a period of one year, the data series clearly demonstrate a sufficient stability.

⁽⁶⁾ SO₂ emissions measurements from SRU may be replaced by a continuous material balance or other relevant process parameter monitoring, provided appropriate measurements of SRU efficiency are based on periodic (e.g. once every 2 years) plant performance tests.

⁽⁷⁾ Antimony (Sb) is monitored only in catalytic cracking units when Sb injection is used in the process (e.g. for metals passivation).

⁽⁸⁾ With the exception of combustion units firing only gaseous fuels.

BAT 5. BAT is to monitor the relevant process parameters linked to pollutant emissions, at catalytic cracking and combustion units by using appropriate techniques and with at least the frequency given below.

| Description | Minimum frequency |
|---|---|
| Monitoring of parameters linked to pollutant emissions, e.g. O ₂ content in flue-gas, N and S content in fuel or feed ⁽¹⁾ | Continuous for O ₂ content. For N and S content, periodic at a frequency based on significant fuel/feed changes |
| ⁽¹⁾ N and S monitoring in fuel or feed may not be necessary when continuous emission measurements of NO _x and SO ₂ are carried out at the stack. | |

BAT 6. BAT is to monitor diffuse VOC emissions to air from the entire site by using all of the following techniques:

- i. sniffing methods associated with correlation curves for key equipment;
- ii. optical gas imaging techniques;
- iii. calculations of chronic emissions based on emissions factors periodically (e.g. once every two years) validated by measurements.

The screening and quantification of site emissions by periodic campaigns with optical absorption-based techniques, such as differential absorption light detection and ranging (DIAL) or solar occultation flux (SOF) is a useful complementary technique.

Description

See Section 5.20.6.

5.1.5 Operation of waste gas treatment systems

BAT 7. In order to prevent or reduce emissions to air, BAT is to operate the acid gas removal units, sulphur recovery units and all other waste gas treatment systems with a high availability and at optimal capacity.

Description

Special procedures can be defined for specific operating conditions, in particular:

- i. during start-up and shutdown operations;
- ii. during other circumstances that could affect the proper functioning of the systems (e.g. regular and extraordinary maintenance work and cleaning operations of the units and/or of the waste gas treatment system);
- iii. in case of insufficient waste gas flow or temperature which prevents the use of the waste gas treatment system at full capacity.

BAT 8. In order to prevent and reduce ammonia (NH₃) emissions to air when applying selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) techniques, BAT is to maintain suitable operating conditions of the SCR or SNCR waste gas treatment systems, with the aim of limiting emissions of unreacted NH₃.

BAT-associated emission levels: See Table 5.2.

Table 5.2: BAT-associated emission levels for ammonia (NH₃) emissions to air for a combustion or process unit where SCR or SNCR techniques are used

| Parameter | BAT-AEL (monthly average) mg/Nm ³ |
|---|--|
| Ammonia expressed as NH ₃ | <5 – 15 ⁽¹⁾ ⁽²⁾ |
| ⁽¹⁾ The higher end of the range is associated with higher inlet NO _x concentrations, higher NO _x reduction rates and the ageing of the catalyst. ⁽²⁾ The lower end of the range is associated with the use of the SCR technique. | |

BAT 9. In order to prevent and reduce emissions to air when using a sour water steam stripping unit, BAT is to route the acid off-gases from this unit to an SRU or any equivalent gas treatment system.

It is not BAT to directly incinerate the untreated sour water stripping gases.

5.1.6 Monitoring of emissions to water

BAT 10. BAT is to monitor emissions to water by using the monitoring techniques with at least the frequency given in Table 5.3 and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

5.1.7 Emissions to water

BAT 11. In order to reduce water consumption and the volume of contaminated water, BAT is to use all of the techniques given below.

| Technique | Description | Applicability |
|--|--|---|
| i. Water stream integration | Reduction of process water produced at the unit level prior to discharge by the internal reuse of water streams from e.g. cooling, condensates, especially for use in crude desalting | Generally applicable for new units. For existing units, applicability may require a complete rebuilding of the unit or the installation |
| ii. Water and drainage system for segregation of contaminated water streams | Design of an industrial site to optimise water management, where each stream is treated as appropriate, by e.g. routing generated sour water (from distillation, cracking, coking units, etc.) to appropriate pretreatment, such as a stripping unit | Generally applicable for new units. For existing units, applicability may require a complete rebuilding of the unit or the installation |
| iii. Segregation of non-contaminated water streams (e.g. once-through cooling, rain water) | Design of a site in order to avoid sending non-contaminated water to general waste water treatment and to have a separate release after possible reuse for this type of stream | Generally applicable for new units. For existing units, applicability may require a complete rebuilding of the unit or the installation |
| iv. Prevention of spillages and leaks | Practices that include the utilisation of special procedures and/or temporary equipment to maintain performances when necessary to manage special circumstances such as spills, loss of containment, etc. | Generally applicable |

BAT 12. In order to reduce the emission load of pollutants in the waste water discharge to the receiving water body, BAT is to remove insoluble and soluble polluting substances by using all of the techniques given below.

| Technique | Description | Applicability |
|--|--------------------|----------------------|
| i. Removal of insoluble substances by recovering oil | See Section 5.21.2 | Generally applicable |
| ii. Removal of insoluble substances by recovering suspended solids and dispersed oil | See Section 5.21.2 | Generally applicable |
| iii. Removal of soluble substances including biological treatment and clarification | See Section 5.21.2 | Generally applicable |

BAT-associated emission levels: See Table 5.3.

BAT 13. When further removal of organic substances or nitrogen is needed, BAT is to use an additional treatment step as described in Section 5.21.2.

Table 5.3: BAT-associated emission levels for direct waste water discharges from the refining of mineral oil and gas and monitoring frequencies associated with BAT ⁽¹⁾

| Parameter | Unit | BAT-AEL (yearly average) | Monitoring ⁽²⁾ frequency and analytical method (standard) |
|--|------|--|--|
| Hydrocarbon oil index (HOI) | mg/l | 0.1 – 2.5 | Daily EN 9377- 2 ⁽³⁾ |
| Total suspended solids (TSS) | mg/l | 5 – 25 | Daily |
| Chemical oxygen demand (COD) ⁽⁴⁾ | mg/l | 30 – 125 | Daily |
| BOD ₅ | mg/l | No BAT-AEL | Weekly |
| Total nitrogen ⁽⁵⁾ , expressed as N | mg/l | 1 – 25 ⁽⁶⁾ | Daily |
| Lead, expressed as Pb | mg/l | 0.005 – 0.030 | Quarterly |
| Cadmium, expressed as Cd | mg/l | 0.002 – 0.008 | Quarterly |
| Nickel, expressed as Ni | mg/l | 0.005 – 0.100 | Quarterly |
| Mercury expressed as Hg | mg/l | 0.0001 – 0.001 | Quarterly |
| Vanadium | mg/l | No BAT-AEL | Quarterly |
| Phenol Index | mg/l | No BAT-AEL | Monthly EN 14402 |
| Benzene, toluene, ethyl benzene, xylene (BTEX) | mg/l | Benzene: 0.001 – 0.050 No BAT-AEL for T, E, X | Monthly |

⁽¹⁾ Not all parameters and sampling frequencies are applicable to effluent from gas refining sites.
⁽²⁾ Refers to a flow-proportional composite sample taken over a period of 24 hours or, provided that sufficient flow stability is demonstrated, a time-proportional sample.
⁽³⁾ Moving from the current method to EN 9377-2 may require an adaptation period.
⁽⁴⁾ Where on-site correlation is available, COD may be replaced by TOC. The correlation between COD and TOC should be elaborated on a case-by-case basis. TOC monitoring would be the preferred option because it does not rely on the use of very toxic compounds.
⁽⁵⁾ Where total-nitrogen is the amount of total Kjeldahl nitrogen (TKN), nitrates and nitrites.
⁽⁶⁾ When nitrification/denitrification is used, levels below 15 mg/l can be achieved.

5.1.8 Waste generation and management

BAT 14. In order to prevent or, where that is not practicable, to reduce waste generation, BAT is to adopt and implement a waste management plan that, in order of priority, ensures that waste is prepared for reuse, recycling, recovery or disposal.

BAT 15. In order to reduce the amount of sludge to be treated or disposed of, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|--------------------------------------|---|---|
| i. Sludge pretreatment | Prior to final treatment (e.g. in a fluidised bed incinerator), the sludges are dewatered and/or de-oiled (by e.g. centrifugal decanters or steam dryers) to reduce their volume and to recover oil from slop equipment | Generally applicable |
| ii. Reuse of sludge in process units | Certain types of sludge (e.g. oily sludge) can be processed in units (e.g. coking) as part of the feed due to their oil content | Applicability is restricted to sludges that can fulfil the requirements to be processed in units with appropriate treatment |

BAT 16. In order to reduce the generation of spent solid catalyst waste, BAT is to use one or a combination of the techniques given below.

| Technique | Description |
|--|---|
| i. Spent solid catalyst management | Scheduled and safe handling of the materials used as catalyst (e.g. by contractors) in order to recover or reuse them in off-site facilities. These operations depend on the type of catalyst and process |
| ii. Removal of catalyst from slurry decant oil | Decanted oil sludge from process units (e.g. FCC unit) can contain significant concentrations of catalyst fines. These fines need to be separated prior to the reuse of decant oil as a feedstock |

5.1.9 Noise

BAT 17. In order to prevent or reduce noise, BAT is to use one or a combination of the techniques given below:

- i. make an environmental noise assessment and formulate a noise management plan as appropriate to the local environment;
- ii. enclose noisy equipment/operation in a separate structure/unit;
- iii. use embankments to screen the source of noise;
- iv. use noise protection walls.

5.1.10 BAT conclusions for integrated refinery management

BAT 18. In order to prevent or reduce diffuse VOC emissions, BAT is to apply the techniques given below.

| Technique | Description | Applicability |
|--|--|---|
| I. Techniques related to plant design | <ul style="list-style-type: none"> i. limiting the number of potential emission sources ii. maximising inherent process containment features iii. selecting high integrity equipment iv. facilitating monitoring and maintenance activities by ensuring access to potentially leaking components | Applicability may be limited for existing units |
| II. Techniques related to plant installation and commissioning | <ul style="list-style-type: none"> i. well-defined procedures for construction and assembly ii. robust commissioning and hand-over procedures to ensure that the plant is installed in line with the design requirements | Applicability may be limited for existing units |
| III. Techniques related to plant operation | Use of a risk-based leak detection and repair (LDAR) programme in order to identify leaking components, and to repair these leaks. See Section 5.20.6 | Generally applicable |

5.2 BAT conclusions for the alkylation process

5.2.1 Hydrofluoric acid alkylation process

BAT 19. In order to prevent hydrofluoric acid (HF) emissions to air from the hydrofluoric acid alkylation process, BAT is to use wet scrubbing with alkaline solution to treat incondensable gas streams prior to venting to flare.

Description

See Section 5.20.3.

Applicability:

The technique is generally applicable. Safety requirements, due to the hazardous nature of hydrofluoric acid, are to be considered.

BAT 20. In order to reduce emissions to water from the hydrofluoric acid alkylation process, BAT is to use a combination of the techniques given below.

| Technique | Description | Applicability |
|--------------------------------------|---|--|
| i. Precipitation/Neutralisation step | Precipitation (with, e.g. calcium or aluminium-based additives) or neutralisation (where the effluent is indirectly neutralised with potassium hydroxide (KOH)) | Generally applicable. Safety requirements due to the hazardous nature of hydrofluoric acid (HF) are to be considered |
| ii. Separation step | The insoluble compounds produced at the first step (e.g. CaF ₂ or AlF ₃) are separated in e.g. a settlement basin | Generally applicable |

5.2.2 Sulphuric acid alkylation process

BAT 21. In order to reduce the emissions to water from the sulphuric acid alkylation process, BAT is to reduce the use of sulphuric acid by regenerating the spent acid and to neutralise waste water generated by this process before routing to waste water treatment.

5.3 BAT conclusions for base oil production processes

BAT 22. In order to prevent and reduce the emissions of hazardous substances to air and water from base oil production processes, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|--|---|---|
| i. Closed process with a solvent recovery | Process where the solvent, after being used during base oil manufacturing (e.g. in extraction, dewaxing units), is recovered through distillation and stripping steps. See Section 5.20.7 | Generally applicable |
| ii. Multi-effect extraction solvent-based process | Solvent extraction process including several stages of evaporation (e.g. double or triple effect) for a lower loss of containment | Generally applicable to new units. The use of a triple effect process may be restricted to non-fouling feed stocks |
| iii. Extraction unit processes using less hazardous substances | Design (new plants) or implement changes (into existing) so that the plant operates a solvent extraction process with the use of a less hazardous solvent: e.g. converting furfural or phenol extraction into the n-methylpyrrolidone (NMP) process | Generally applicable to new units. Converting existing units to another solvent-based process with different physico-chemical properties may require substantial modifications |
| iv. Catalytic processes based on hydrogenation | Processes based on conversion of undesired compounds via catalytic hydrogenation similar to hydrotreatment. See Section 5.20.3 (Hydrotreatment) | Generally applicable to new units |

5.4 BAT conclusions for the bitumen production process

BAT 23. In order to prevent and reduce emissions to air from the bitumen production process, BAT is to treat the gaseous overhead by using one of the techniques given below.

| Technique | Description | Applicability |
|--|--------------------|---|
| i. Thermal oxidation of gaseous overhead over 800 °C | See Section 5.20.6 | Generally applicable for the bitumen blowing unit |
| ii. Wet scrubbing of gaseous overhead | See Section 5.20.3 | Generally applicable for the bitumen blowing unit |

5.5 BAT conclusions for the fluid catalytic cracking process

BAT 24. In order to prevent or reduce NO_x emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below.

I. Primary or process-related techniques, such as:

| Technique | Description | Applicability |
|--|---|---|
| Process optimisation and use of promoters or additives | | |
| i. Process optimisation | Combination of operating conditions or practices aimed at reducing NO _x formation, e.g. lowering the excess oxygen in the flue-gas in full combustion mode, air staging of the CO boiler in partial combustion mode, provided that the CO boiler is appropriately designed | Generally applicable |
| ii. Low-NO _x CO oxidation promoters | Use of a substance that selectively promotes the combustion of CO only and prevents the oxidation of the nitrogen that contains intermediates to NO _x ; e.g. non-platinum promoters | Applicable only in full combustion mode for the substitution of platinum-based CO promoters. Appropriate distribution of air in the regenerator may be required to obtain the maximum benefit |
| iii. Specific additives for NO _x reduction | Use of specific catalytic additives for enhancing the reduction of NO by CO | Applicable only in full combustion mode in an appropriate design and with achievable oxygen excess. The applicability of copper-based NO _x reduction additives may be limited by the gas compressor capacity |

II. Secondary or end-of-pipe techniques, such as:

| Technique | Description | Applicability |
|--|--------------------|--|
| i. Selective catalytic reduction (SCR) | See Section 5.20.2 | To avoid potential fouling downstream, additional filtering might be required upstream of the SCR. For existing units, the applicability may be limited by space availability |
| ii. Selective non-catalytic reduction (SNCR) | See Section 5.20.2 | For partial combustion FCCs with CO boilers, a sufficient residence time at the appropriate temperature is required. For full combustion FCCs without auxiliary boilers, additional fuel injection (e.g. hydrogen) may be required to match a lower temperature window |
| iii. Low temperature oxidation | See Section 5.20.2 | Need for additional scrubbing capacity. Ozone generation and the associated risk management need to be properly addressed. The applicability may be limited by the need for additional waste water treatment and related cross-media effects (e.g. nitrate emissions) and by an insufficient supply of liquid oxygen (for ozone generation). The applicability of the technique may be limited by space availability |

BAT-associated emission levels: See Table 5.4.

Table 5.4: BAT- associated emission levels for NO_x emissions to air from the regenerator in the catalytic cracking process

| Parameter | Type of unit/combustion mode | BAT-AEL (monthly average) mg/Nm ³ |
|--|---------------------------------------|--|
| NO _x , expressed as NO ₂ | New unit/all combustion mode | <30 – 100 |
| | Existing unit/full combustion mode | <100 – 300 (¹) |
| | Existing unit/partial combustion mode | 100 – 400 (¹) |
| ⁽¹⁾ When antimony (Sb) injection is used for metal passivation, NO _x levels up to 700 mg/Nm ³ may occur. The lower end of the range can be achieved by using the SCR technique. | | |

The associated monitoring is in BAT 4.

BAT 25. In order to reduce dust and metals emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below.

I. Primary or process-related techniques, such as:

| Technique | Description | Applicability |
|---|---|--|
| i. Use of an attrition-resistant catalyst | Selection of catalyst substance that is able to resist abrasion and fragmentation in order to reduce dust emissions | Generally applicable provided the activity and selectivity of the catalyst are sufficient |
| ii. Use of low sulphur feedstock (e.g. by feedstock selection or by hydrotreatment of feed) | Feedstock selection favours low sulphur feedstocks among the possible sources to be processed at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the feed. See Section 5.20.3 | Requires sufficient availability of low sulphur feedstocks, hydrogen production and hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units) |

II. Secondary or end-of-pipe techniques, such as:

| Technique | Description | Applicability |
|-------------------------------------|--------------------|--|
| i. Electrostatic precipitator (ESP) | See Section 5.20.1 | For existing units, the applicability may be limited by space availability |
| ii. Multistage cyclone separators | See Section 5.20.1 | Generally applicable |
| iii. Third stage blowback filter | See Section 5.20.1 | Applicability may be restricted |
| iv. Wet scrubbing | See Section 5.20.3 | The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. For existing units, the applicability may be limited by space availability |

BAT-associated emission levels: See Table 5.5.

Table 5.5: BAT-associated emission levels for dust emissions to air from the regenerator in the catalytic cracking process

| Parameter | Type of unit | BAT-AEL (monthly average) ⁽¹⁾ mg/Nm ³ |
|---|---------------|---|
| Dust | New unit | 10 – 25 |
| | Existing unit | 10 – 50 ⁽²⁾ |
| ⁽¹⁾ Soot blowing in CO boiler and through the gas cooler is excluded. ⁽²⁾ The lower end of the range can be achieved with a 4-field ESP. | | |

The associated monitoring is in BAT 4.

BAT 26. In order to prevent or reduce SO_x emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below.

I. Primary or process-related techniques, such as:

| Technique | Description | Applicability |
|---|--|--|
| i. Use of SO _x reducing catalysts additives | Use of a substance that transfers the sulphur associated with coke from the regenerator back to the reactor. See description in 5.20.3 | Applicability may be restricted by regenerator conditions design. Requires appropriate hydrogen sulphide abatement capacity (e.g. SRU) |
| ii. Use of low sulphur feedstock (e.g. by feedstock selection or by hydrotreatment of the feed) | Feedstock selection favours low sulphur feedstocks among the possible sources to be processed at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the feed. See description in 5.20.3 | Requires sufficient availability of low sulphur feedstocks, hydrogen production and hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units) |

II. Secondary or end-of-pipe techniques, such as:

| Techniques | Description | Applicability |
|-------------------------------|---|---|
| i. Non-regenerative scrubbing | Wet scrubbing or seawater scrubbing. See Section 5.20.3 | The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. For existing units, the applicability may be limited by space availability |
| ii. Regenerative scrubbing | Use of a specific SO _x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused. See Section 5.20.3 | The applicability is limited to the case where regenerated by-products can be sold. For existing units, the applicability may be limited by the existing sulphur recovery capacity as well as by space availability |

BAT-associated emission levels: See Table 5.6.

Table 5.6: BAT-associated emission levels for SO₂ emissions to air from the regenerator in the catalytic cracking process

| Parameter | Type of unit/mode | BAT-AEL (monthly average) mg/Nm ³ |
|---|-----------------------------------|--|
| SO ₂ | New unit | ≤ 300 |
| | Existing units/full combustion | <100 – 800 ⁽¹⁾ |
| | Existing units/partial combustion | 100 – 1 200 ⁽¹⁾ |
| ⁽¹⁾ Where selection of low sulphur (e.g. <0.5 % w/w) feed (or hydrotreatment) and/or scrubbing is applicable, for all combustion modes: the upper end of the BAT-AEL range is ≤ 600 mg/Nm ³ . | | |

The associated monitoring is in BAT 4.

BAT 27. In order to reduce carbon monoxide (CO) emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|---|--------------------|---|
| i. Combustion operation control | See Section 5.20.5 | Generally applicable |
| ii. Catalysts with carbon monoxide (CO) oxidation promoters | See Section 5.20.5 | Generally applicable only for full combustion mode |
| iii. Carbon monoxide (CO) boiler | See Section 5.20.5 | Generally applicable only for partial combustion mode |

BAT-associated emission levels: See Table 5.7.

Table 5.7: BAT-associated emission levels for carbon monoxide emissions to air from the regenerator in the catalytic cracking process for partial combustion mode

| Parameter | Combustion mode | BAT-AEL (monthly average) mg/Nm ³ |
|---|-------------------------|--|
| Carbon monoxide, expressed as CO | Partial combustion mode | ≤ 100 ⁽¹⁾ |
| ⁽¹⁾ May not be achievable when not operating the CO boiler at full load. | | |

The associated monitoring is in BAT 4.

5.6 BAT conclusions for the catalytic reforming process

BAT 28. In order to reduce emissions of polychlorinated dibenzodioxins/furans (PCDD/F) to air from the catalytic reforming unit, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|--|--|--|
| i. Choice of the catalyst promoter | Use of catalyst promoter in order to minimise polychlorinated dibenzodioxins/furans (PCDD/F) formation during regeneration. See Section 5.20.7 | Generally applicable |
| ii. Treatment of the regeneration flue-gas | | |
| a. Regeneration gas recycling loop with adsorption bed | Waste gas from the regeneration step is treated to remove chlorinated compounds (e.g. dioxins) | Generally applicable to new units. For existing units the applicability may depend on the current regeneration unit design |
| b. Wet scrubbing | See Section 5.20.3 | Not applicable to semi-regenerative reformers |
| c. Electrostatic precipitator (ESP) | See Section 5.20.1 | Not applicable to semi-regenerative reformers |

5.7 BAT conclusions for the coking process

BAT 29. In order to reduce emissions to air from coking production processes, BAT is to use one or a combination of the techniques given below:

Primary or process-related techniques, such as:

| Technique | Description | Applicability |
|--|---|--|
| i. Collection and recycling of coke fines | Systematic collection and recycling of coke fines generated during the whole coking process (drilling, handling, crushing, cooling, etc.) | Generally applicable |
| ii. Handling and storage of coke according to BAT 3 | See BAT 3 | Generally applicable |
| iii. Use of a closed blowdown system | Arrestment system for pressure relief from the coke drums | Generally applicable |
| iv. Recovery of gas (including the venting prior to the drum being opened to atmosphere) as a component of refinery fuel gas (RFG) | Carrying venting from the coke drum to the gas compressor to recover as RFG, rather than flaring. For the flexicoking process, a conversion step (to convert the carbonyl sulphide (COS) into H ₂ S) is needed prior to treating the gas from the coking unit | For existing units, the applicability of the techniques may be limited by space availability |

BAT 30. In order to reduce NO_x emissions to air from the calcining of green coke process, BAT is to use selective non-catalytic reduction (SNCR).

Description: See Section 5.20.2.

Applicability

The applicability of the SNCR technique (especially with respect to residence time and temperature window) may be restricted due to the specificity of the calcining process.

BAT 31. In order to reduce SO_x emissions to air from the calcining of green coke process, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|-------------------------------|--|--|
| i. Non-regenerative scrubbing | Wet scrubbing or seawater scrubbing. See Section 5.20.3 | The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. For existing units, the applicability may be limited by space availability |
| ii. Regenerative scrubbing | Use of a specific SO _x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused. See Section 5.20.3 | The applicability is limited to the case where regenerated by-products can be sold. For existing units, the applicability may be limited by the existing sulphur recovery capacity as well as by space availability |

BAT 32. In order to reduce dust emissions to air from the calcining of green coke process, BAT is to use a combination of the techniques given below.

| Technique | Description | Applicability |
|-------------------------------------|--------------------|--|
| i. Electrostatic precipitator (ESP) | See Section 5.20.1 | For existing units, the applicability may be limited by space availability. For graphite and anode coke calcining production, the applicability may be restricted due to the high resistivity of the coke particles |
| ii. Multistage cyclone separators | See Section 5.20.1 | Generally applicable |

BAT-associated emission levels: See Table 5.8.

Table 5.8: BAT-associated emission levels for dust emissions to air from a unit for the calcining of green coke

| Parameter | BAT-AEL (monthly average) mg/Nm ³ |
|---|--|
| Dust | 10 – 50 ⁽¹⁾ ⁽²⁾ |
| ⁽¹⁾ The lower end of the range can be achieved with a 4-field ESP. | |
| ⁽²⁾ When an ESP is not applicable, values of up to 150 mg/Nm ³ may occur. | |

The associated monitoring is in BAT 4.

5.8 BAT conclusions for the desalting process

BAT 33. In order to reduce water consumption and emissions to water from the desalting process, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|--|---|--------------------------|
| i. Recycling water and optimisation of the desalting process | An ensemble of good desalting practices aiming at increasing the efficiency of the desalter and reducing wash water usage e.g. using low shear mixing devices, low water pressure. It includes the management of key parameters for washing (e.g. good mixing) and separation (e.g. pH, density, viscosity, electric field potential for coalescence) steps | Generally applicable |
| ii. Multistage desalter | Multistage desalters operate with water addition and dehydration, repeated through two stages or more for achieving a better efficiency in the separation and therefore less corrosion in further processes | Applicable for new units |
| iii. Additional separation step | An additional enhanced oil/water and solid/water separation designed for reducing the charge of oil to the waste water treatment plant and recycling it to the process. This includes, e.g. settling drum, the use of optimum interface level controllers | Generally applicable |

5.9 BAT conclusions for the combustion units

BAT 34. In order to prevent or reduce NO_x emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below.

I. Primary or process-related techniques, such as:

| Technique | Description | Applicability |
|---|--|--|
| i. Selection or treatment of fuel | | |
| (a) Use of gas to replace liquid fuel | Gas generally contains less nitrogen than liquid and its combustion leads to a lower level of NO _x emissions. See Section 5.20.3 | The applicability may be limited by the constraints associated with the availability of low sulphur gas fuels, which may be impacted by the energy policy of the Member State |
| (b) Use of low nitrogen refinery fuel oil (RFO) e.g. by RFO selection or by hydrotreatment of RFO | Refinery fuel oil selection favours low nitrogen liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the fuel. See Section 5.20.3 | Applicability is limited by the availability of low nitrogen liquid fuels, hydrogen production and hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units) |
| ii. Combustion modifications | | |
| (a) Staged combustion: • air staging • fuel staging | See Section 5.20.2 | Fuel staging for mixed or liquid firing may require a specific burner design |
| (b) Optimisation of combustion | See Section 5.20.2 | Generally applicable |
| (c) Flue-gas recirculation | See Section 5.20.2 | Applicable through the use of specific burners with internal recirculation of the flue-gas. The applicability may be restricted to retrofitting external flue-gas recirculation to units with a forced/induced draught mode of operation |
| (d) Diluent injection | See Section 5.20.2 | Generally applicable for gas turbines where appropriate inert diluents are available |
| (e) Use of low-NO _x burners (LNB) | See Section 5.20.2 | Generally applicable for new units taking into account the fuel-specific limitation (e.g. for heavy oil). For existing units, applicability may be restricted by the complexity caused by site-specific conditions e.g. furnaces design, surrounding devices. In very specific cases, substantial modifications may be required. The applicability may be restricted for furnaces in the delayed coking process, due to possible coke generation in the furnaces. In gas turbines, the applicability is restricted to low hydrogen content fuels (generally <10 %) |

II. Secondary or end-of-pipe techniques, such as:

| Technique | Description | Applicability |
|--|--------------------|--|
| i. Selective catalytic reduction (SCR) | See Section 5.20.2 | Generally applicable for new units. For existing units, the applicability may be constrained due to the requirements for significant space and optimal reactant injection |
| ii. Selective non-catalytic reduction (SNCR) | See Section 5.20.2 | Generally applicable for new units. For existing units, the applicability may be constrained by the requirement for the temperature window and the residence time to be reached by reactant injection |
| iii. Low temperature oxidation | See Section 5.20.2 | The applicability may be limited by the need for additional scrubbing capacity and by the fact that ozone generation and the associated risk management need to be properly addressed. The applicability may be limited by the need for additional waste water treatment and related cross-media effects (e.g. nitrate emissions) and by an insufficient supply of liquid oxygen (for ozone generation). For existing units, the applicability of the technique may be limited by space availability |
| iv. SNO _x combined technique | See Section 5.20.4 | Applicable only for high flue-gas (e.g. > 800 000 Nm ³ /h) flow and when combined NO _x and SO _x abatement is needed |

BAT-associated emission levels: See Table 5.9, Table 5.10 and Table 5.11.

Table 5.9: BAT-associated emission levels for NO_x emissions to air from a gas turbine

| Parameter | Type of equipment | BAT-AEL ⁽¹⁾ (monthly average) mg/Nm ³ at 15 % O ₂ |
|---|---|--|
| NO _x expressed as NO ₂ | Gas turbine (including combined cycle gas turbines – CCGT) and integrated gasification gas cycle (IGCC) | 40 – 120 (existing turbine) |
| | | 20 – 50 (new turbine) ⁽²⁾ |
| ⁽¹⁾ BAT-AEL refers to combined emissions from the gas turbine and the supplementary firing recovery boiler, where present. | | |
| ⁽²⁾ For fuel with high H ₂ content (i.e. above 10 %), the upper end of the range is 75 mg/Nm ³ . | | |

The associated monitoring is in BAT 4.

Table 5.10: BAT-associated emission levels for NO_x emissions to air from a gas-fired combustion unit, with the exception of gas turbines

| Parameter | Type of combustion | BAT-AEL (monthly average) mg/Nm ³ |
|--|--------------------|--|
| NO _x expressed as NO ₂ | Gas firing | 30 – 150 for existing unit ⁽¹⁾ |
| | | 30 – 100 for new unit |
| ⁽¹⁾ For an existing unit using high air pre-heat (i.e. >200 °C) or with H ₂ content in the fuel gas higher than 50 %, the upper end of the BAT-AEL range is 200 mg/Nm ³ . | | |

The associated monitoring is in BAT 4.

Table 5.11: BAT-associated emission levels for NO_x emissions to air from a multi-fuel fired combustion unit with the exception of gas turbines

| Parameter | Type of combustion | BAT-AEL (monthly average) mg/Nm ³ |
|---|----------------------------------|---|
| NO _x expressed as NO ₂ | Multi-fuel fired combustion unit | 30 – 300 for existing unit ⁽¹⁾ ⁽²⁾ |
| ⁽¹⁾ For existing units <100 MW firing fuel oil with a nitrogen content higher than 0.5 % (w/w) or with liquid firing >50 % or using air preheating, values up to 450 mg/Nm ³ may occur. | | |
| ⁽²⁾ The lower end of the range can be achieved by using the SCR technique. | | |

The associated monitoring is in BAT 4.

BAT 35. In order to prevent or reduce dust and metal emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below.

I. Primary or process-related techniques, such as:

| Technique | Description | Applicability |
|--|--|--|
| i. Selection or treatment of fuel | | |
| (a) Use of gas to replace liquid fuel | Gas instead of liquid combustion leads to lower level of dust emissions See Section 5.20.3 | The applicability may be limited by the constraints associated with the availability of low sulphur fuels such as natural gas, which may be impacted by the energy policy of the Member State |
| (b) Use of low sulphur refinery fuel oil (RFO) e.g. by RFO selection or by hydrotreatment of RFO | Refinery fuel oil selection favours low sulphur liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the fuel. See Section 5.20.3 | The applicability may be limited by the availability of low sulphur liquid fuels, hydrogen production and the hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units) |
| ii. Combustion modifications | | |
| (a) Optimisation of combustion | See Section 5.20.2 | Generally applicable to all types of combustion |
| (b) Atomisation of liquid fuel | Use of high pressure to reduce the droplet size of liquid fuel. Recent optimal burner designs generally include steam atomisation | Generally applicable to liquid fuel firing |

II. Secondary or end-of-pipe techniques, such as:

| Technique | Description | Applicability |
|-------------------------------------|--------------------|---|
| i. Electrostatic precipitator (ESP) | See Section 5.20.1 | For existing units, the applicability may be limited by space availability |
| ii. Third stage blowback filter | See Section 5.20.1 | Generally applicable |
| iii. Wet scrubbing | See Section 5.20.3 | The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with a high level of salt) cannot be reused or appropriately disposed of. For existing units, the applicability of the technique may be limited by space availability |
| iv. Centrifugal washers | See Section 5.20.1 | Generally applicable |

BAT-associated emission levels: See Table 5.12.

Table 5.12: BAT-associated emission levels for dust emissions to air from a multi-fuel fired combustion unit with the exception of gas turbines

| Parameter | Type of combustion | BAT-AEL (monthly average) mg/Nm ³ |
|--|--------------------|---|
| Dust | Multi-fuel firing | 5 – 50 for existing unit ⁽¹⁾ ⁽²⁾ |
| | | 5 – 25 for new unit <50 MW |
| ⁽¹⁾ The lower end of the range is achievable for units with the use of end-of-pipe techniques. ⁽²⁾ The upper end of the range refers to the use of a high percentage of oil burning and where only primary techniques are applicable. | | |

The associated monitoring is in BAT 4.

BAT 36. In order to prevent or reduce SO_x emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

- I. Primary or process-related techniques based on a selection or a treatment of the fuel, such as:

| Technique | Description | Applicability |
|---|--|--|
| i. Use of gas to replace liquid fuel | See Section 5.20.3 | The applicability may be limited by the constraints associated with the availability of low sulphur fuels such as natural gas, which may be impacted by the energy policy of the Member State |
| ii. Treatment of refinery fuel gas (RFG) | Residual H ₂ S concentration in RFG depends on the treatment process parameter, e.g. the amine-scrubbing pressure. See Section 5.20.3 | For low calorific gas containing carbonyl sulphide (COS) e.g. from coking units, a converter may be required prior to H ₂ S removal |
| iii. Use of low sulphur refinery fuel oil (RFO) e.g. by RFO selection or by hydrotreatment of RFO | Refinery fuel oil selection favours low sulphur liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the fuel. See Section 5.20.3 | The applicability is limited by the availability of low sulphur liquid fuels, hydrogen production and the hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units) |

- II. Secondary or end-of-pipe techniques:

| Technique | Description | Applicability |
|--|--|---|
| i. Non-regenerative scrubbing | Wet scrubbing or seawater scrubbing. See Section 5.20.3 | The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. For existing units, the applicability of the technique may be limited by space availability |
| ii. Regenerative scrubbing | Use of a specific SO _x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused. See Section 5.20.3 | The applicability is limited to the case where regenerated by-products can be sold. Retrofitting to existing units may be limited by the existing sulphur recovery capacity. For existing units, the applicability of the technique may be limited by space availability |
| iii. SNO _x combined technique | See Section 5.20.4 | Applicable only for high flue-gas (e.g. >800 000 Nm ³ /h) flow and when combined NO _x and SO _x abatement is required |

BAT-associated emission levels: See Table 5.13 and Table 5.14.

Table 5.13: BAT-associated emission levels for SO₂ to air from a combustion unit firing refinery fuel gas (RFG), with the exception of gas turbines

| Parameter | BAT-AEL (monthly average) mg/Nm ³ |
|---|--|
| SO ₂ | 5 – 35 ⁽¹⁾ |
| ⁽¹⁾ In the specific configuration of RFG treatment with a low scrubber operative pressure and with a refinery fuel gas with an H/C molar ratio above 5, the upper end of the BAT-AEL range can be as high as 45 mg/Nm ³ . | |

The associated monitoring is in BAT 4.

Table 5.14: BAT-associated emission levels for SO₂ emissions to air from multi-fuel fired combustion units, with the exception of gas turbines and stationary gas engines

This BAT-AEL refers to the weighted average emissions from existing multi-fuel fired combustion units within the refinery, with the exception of gas turbines and stationary gas engines.

| Parameter | BAT-AEL (monthly average) mg/Nm ³ |
|-----------------|--|
| SO ₂ | 35 – 600 |

The associated monitoring is in BAT 4.

BAT 37. In order to reduce carbon monoxide (CO) emissions to air from the combustion units, BAT is to use a combustion operation control.

Description: See Section 5.20.5.

BAT-associated emission levels: See Table 5.15.

Table 5.15: BAT-associated emission levels for carbon monoxide emissions to air from a combustion unit

| Parameter | BAT-AEL (monthly average) mg/Nm ³ |
|----------------------------------|--|
| Carbon monoxide, expressed as CO | ≤ 100 |

The associated monitoring is in BAT 4.

5.10 BAT conclusions for the etherification process

BAT 38. In order to reduce emissions to air from the etherification process, BAT is to ensure the appropriate treatment of process off-gases by routing them to the refinery fuel gas system.

BAT 39. In order to prevent upset of the biotreatment, BAT is to use a storage tank and an appropriate unit production plan management to control the toxic components dissolved content (e.g. methanol, formic acid, ethers) of the waste water stream prior to final treatment.

5.11 BAT conclusions for the isomerisation process

BAT 40. In order to reduce emissions to air of chlorinated compounds, BAT is to optimise the use of chlorinated organic compounds used to maintain catalyst activity when such a process is in place or to use non-chlorinated catalytic systems.

5.12 BAT conclusions for the natural gas refinery

BAT 41. In order to reduce sulphur dioxide emissions to air from the natural gas plant, BAT is to apply BAT 54.

BAT 42. In order to reduce nitrogen oxides (NO_x) emissions to air from the natural gas plant, BAT is to apply BAT 34.

BAT 43. In order to prevent emissions of mercury when present in raw natural gas, BAT is to remove the mercury and recover the mercury-containing sludge for waste disposal.

5.13 BAT conclusions for the distillation process

BAT 44. In order to prevent or reduce waste water flow generation from the distillation process, BAT is to use liquid ring vacuum pumps or surface condensers.

Applicability

May not be applicable in some retrofit cases. For new units, vacuum pumps, either in or not in combination with steam ejectors, may be needed to achieve a high vacuum (10 mm Hg). Also, a spare should be available in case the vacuum pump fails.

BAT 45. In order to prevent or reduce water pollution from the distillation process, BAT is to route sour water to the stripping unit.

BAT 46. In order to prevent or reduce emissions to air from distillation units, BAT is to ensure the appropriate treatment of process off-gases, especially incondensable off-gases, by acid gas removal prior to further use.

Applicability

Generally applicable for crude and vacuum distillation units. May not be applicable for stand-alone lubricant and bitumen refineries with emissions of less than 1 t/d of sulphur compounds. In specific refinery configurations, applicability may be restricted, due to the need for e.g. large piping, compressors or additional amine treating capacity.

5.14 BAT conclusions for the products treatment process

BAT 47. In order to reduce emissions to air from the products treatment process, BAT is to ensure the appropriate disposal of off-gases, especially odorous spent air from sweetening units, by routing them to destruction, e.g. by incineration.

Applicability

Generally applicable to products treatment processes where the gas streams can be safely processed to the destruction units. May not be applicable to sweetening units, due to safety reasons.

BAT 48. In order to reduce waste and waste water generation when a products treatment process using caustic is in place, BAT is to use cascading caustic solution and a global management of spent caustic, including recycling after appropriate treatment, e.g. by stripping.

5.15 BAT conclusions for storage and handling processes

BAT 49. In order to reduce VOC emissions to air from the storage of volatile liquid hydrocarbon compounds, BAT is to use floating roof storage tanks equipped with high efficiency seals or a fixed roof tank connected to a vapour recovery system.

Description

High efficiency seals are specific devices for limiting losses of vapour, e.g. improved primary seals, additional multiple (secondary or tertiary) seals (according to quantity emitted).

Applicability

The applicability of high efficiency seals may be restricted for retrofitting tertiary seals in existing tanks.

BAT 50. In order to reduce VOC emissions to air from the storage of volatile liquid hydrocarbon compounds, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|-----------------------------------|--|---|
| i. Manual crude oil tank cleaning | Oil tank cleaning is performed by workers entering the tank and removing sludge manually | Generally applicable |
| ii. Use of a closed-loop system | For internal inspections, tanks have to be periodically emptied, cleaned and rendered gas-free. This cleaning includes dissolving the tank bottom. Closed-loop systems that can be combined with end-of-pipe mobile abatement techniques prevent or reduce VOC emissions | The applicability may be limited by e.g. the type of residues, tank roof construction or tank materials |

BAT 51. In order to prevent or reduce emissions to soil and groundwater from the storage of liquid hydrocarbon compounds, BAT is to use one or a combination of the techniques given below.

| Technique | Description | Applicability |
|---|---|---|
| i. Maintenance programme including corrosion monitoring, prevention and control | A management system including leak detection and operational controls to prevent overfilling, inventory control and risk-based inspection procedures on tanks at intervals to prove their integrity, and maintenance to improve tank containment. It also includes a system response to spill consequences to act before spills can reach the groundwater. To be especially reinforced during maintenance periods | Generally applicable |
| ii. Double bottomed tanks | A second impervious bottom that provides a measure of protection against releases from the first material | Generally applicable for new tanks and after overhaul of existing tanks ⁽¹⁾ |
| iii. Impervious membrane liners | A continuous leak barrier under the entire bottom surface of the tank | Generally applicable for new tanks and after an overhaul of existing tanks ⁽¹⁾ |
| iv. Sufficient tank farm bund containment | A tank farm bund is designed to contain large spills potentially caused by a shell rupture or overfilling (for both environmental and safety reasons). Size and associated building rules are generally defined by local regulations | Generally applicable |
| ⁽¹⁾ Techniques ii and iii may not be generally applicable where tanks are dedicated to products that require heat for liquid handling (e.g. bitumen), and where no leak is likely because of solidification. | | |

BAT 52. In order to prevent or reduce VOC emissions to air from loading and unloading operations of volatile liquid hydrocarbon compounds, BAT is to use one or a combination of the techniques given below to achieve a recovery rate of at least 95 %.

| Technique | Description | Applicability ⁽¹⁾ |
|---|--------------------|---|
| Vapour recovery by: i. Condensation ii. Absorption iii. Adsorption iv. Membrane separation v. Hybrid systems | See Section 5.20.6 | Generally applicable to loading/unloading operations where annual throughput is >5 000 m ³ /yr. Not applicable to loading/unloading operations for sea-going vessels with an annual throughput <1 million m ³ /yr |
| ⁽¹⁾ A vapour destruction unit (e.g. by incineration) may be substituted for a vapour recovery unit, if vapour recovery is unsafe or technically impossible because of the volume of return vapour. | | |

BAT-associated emission levels: See Table 5.16.

Table 5.16: BAT-associated emission levels for non-methane VOC and benzene emissions to air from loading and unloading operations of volatile liquid hydrocarbon compounds

| Parameter | BAT-AEL (hourly average) ⁽¹⁾ |
|--|---|
| NMVOC | 0.15 – 10 g/Nm ³ ⁽²⁾ ⁽³⁾ |
| Benzene ⁽³⁾ | <1 mg/Nm ³ |
| ⁽¹⁾ Hourly values in continuous operation expressed and measured according to European Parliament and Council Directive 94/63/EC (OJ L 365, 31.12.1994, p. 24). ⁽²⁾ Lower value achievable with two-stage hybrid systems. Upper value achievable with single-stage adsorption or membrane system. ⁽³⁾ Benzene monitoring may not be necessary where emissions of NMVOC are at the lower end of the range. | |

5.16 BAT conclusions for visbreaking and other thermal processes

BAT 53. In order to reduce emissions to water from visbreaking and other thermal processes, BAT is to ensure the appropriate treatment of waste water streams by applying the techniques of BAT 11.

5.17 BAT conclusions for waste gas sulphur treatment

BAT 54. In order to reduce sulphur emissions to air from off-gases containing hydrogen sulphides (H₂S), BAT is to use all of the techniques given below.

| Technique | Description | Applicability ⁽¹⁾ |
|---|--------------------|--|
| i. Acid gas removal e.g. by amine treating | See Section 5.20.3 | Generally applicable |
| ii. Sulphur recovery units (SRU), e.g. by Claus process | See Section 5.20.3 | Generally applicable |
| iii. Tail gas treatment unit (TGTU) | See Section 5.20.3 | For retrofitting existing SRU, the applicability may be limited by the SRU size and configuration of the units and the type of sulphur recovery process already in place |
| ⁽¹⁾ May not be applicable for stand-alone lubricant or bitumen refineries with a release of sulphur compounds of less than 1 t/d | | |

BAT-associated environmental performance levels (BAT-AEPL): See Table 5.17.

Table 5.17: BAT-associated environmental performance levels for a waste gas sulphur (H₂S) recovery system

| | BAT-associated environmental performance level (monthly average) |
|---|---|
| Acid gas removal | Achieve hydrogen sulphides (H ₂ S) removal in the treated RFG in order to meet gas firing BAT-AEL for BAT 36 |
| Sulphur recovery efficiency ⁽¹⁾ | New unit: 99.5 – >99.9 % |
| | Existing unit: ≥ 98.5 % |
| ⁽¹⁾ Sulphur recovery efficiency is calculated over the whole treatment chain (including SRU and TGTU) as the fraction of sulphur in the feed that is recovered in the sulphur stream routed to the collection pits. When the applied technique does not include a recovery of sulphur (e.g. seawater scrubber), it refers to the sulphur removal efficiency, as the % of sulphur removed by the whole treatment chain. | |

The associated monitoring is described in BAT 4.

5.18 BAT conclusions for flares

BAT 55. In order to prevent emissions to air from flares, BAT is to use flaring only for safety reasons or for non-routine operational conditions (e.g. start-ups, shutdown).

BAT 56. In order to reduce emissions to air from flares when flaring is unavoidable, BAT is to use the techniques given below.

| Technique | Description | Applicability |
|-------------------------------------|--------------------|--|
| i. Correct plant design | See Section 5.20.7 | Applicable to new units. Flare gas recovery system may be retrofitted in existing units |
| ii. Plant management | See Section 5.20.7 | Generally applicable |
| iii. Correct flaring devices design | See Section 5.20.7 | Applicable to new units |
| iv. Monitoring and reporting | See Section 5.20.7 | Generally applicable |

5.19 BAT conclusions for integrated emission management

BAT 57. In order to achieve an overall reduction of NO_x emissions to air from combustion units and fluid catalytic cracking (FCC) units, BAT is to use an integrated emission management technique as an alternative to applying BAT 24 and BAT 34.

Description

The technique consists of managing NO_x emissions from several or all combustion units and FCC units on a refinery site in an integrated manner, by implementing and operating the most appropriate combination of BAT across the different units concerned and monitoring the effectiveness thereof, in such a way that the resulting total emissions are equal to or lower than the emissions that would be achieved through a unit-by-unit application of the BAT-AELs referred to in BAT 24 and BAT 34.

This technique is especially suitable to oil refining sites:

- with a recognised site complexity, multiplicity of combustion and process units interlinked in terms of their feedstock and energy supply;
- with frequent process adjustments required in function of the quality of the crude received;
- with a technical necessity to use a part of process residues as internal fuels, causing frequent adjustments of the fuel mix according to process requirements.

BAT-associated emissions levels: see Table 5.18.

In addition, for each new combustion unit or new FCC unit included in the integrated emission management system, the BAT-AELs set out under BAT 24 and BAT 34 remain applicable.

Table 5.18: BAT-associated emission levels for NO_x emissions to air when applying BAT 57

The BAT-AEL for NO_x emissions from the units concerned by BAT 57, expressed in mg/Nm³ as a monthly average value, is equal to or less than the weighted average of the NO_x concentrations (expressed in mg/Nm³ as a monthly average) that would be achieved by applying in practice at each of those units techniques that would enable the units concerned to meet the following:

- for catalytic cracking process (regenerator) units: the BAT-AEL range set out in Table 5.4 (BAT 24);
- for combustion units burning refinery fuels alone or simultaneously with other fuels: the BAT-AEL ranges set out in Table 5.9, Table 5.10 and Table 5.11 (BAT 34).

This BAT-AEL is expressed by the following formula:

$$\frac{\sum[(\text{flue gas flow rate of the unit concerned}) \times (\text{NO}_x \text{ concentration that would be achieved for that unit})]}{\sum (\text{flue gas flow rate of all units concerned})}$$

Notes:

1. The applicable reference conditions for oxygen are those specified in Table 5.1.
2. The weighing of the emission levels of the individual units is done on the basis of the flue-gas flow rate of the unit concerned, expressed as a monthly average value (Nm³/hour), which is representative for the normal operation of that unit within the refinery installation (applying the reference conditions under Note 1).
3. In case of substantial and structural fuel changes which are affecting the applicable BAT-AEL for a unit or other substantial and structural changes in the nature or functioning

of the units concerned, or in case of their replacement or extension or the addition of combustion units or FCC units, the BAT-AEL defined in Table 5.18 needs to be adjusted accordingly.

Monitoring associated with BAT 57

BAT for monitoring emissions of NO_x under an integrated emission management technique is as in BAT 4, complemented with the following:

- a monitoring plan including a description of the processes monitored, a list of the emission sources and source streams (products, waste gases) monitored for each process and a description of the methodology (calculations, measurements) used and the underlying assumptions and associated level of confidence;
- continuous monitoring of the flue-gas flow rates of the units concerned, either through direct measurement or by an equivalent method;
- a data management system for collecting, processing and reporting all monitoring data needed to determine the emissions from the sources covered by the integrated emission management technique.

BAT 58. In order to achieve an overall reduction of SO₂ emissions to air from combustion units, fluid catalytic cracking (FCC) units and waste gas sulphur recovery units, BAT is to use an integrated emission management technique as an alternative to applying BAT 26, BAT 36 and BAT 54.

Description

The technique consists of managing SO₂ emissions from several or all combustion units, FCC units and waste gas sulphur recovery units on a refinery site in an integrated manner, by implementing and operating the most appropriate combination of BAT across the different units concerned and monitoring the effectiveness thereof, in such a way that the resulting total emissions are equal to or lower than the emissions that would be achieved through a unit-by-unit application of the BAT-AELs referred to in BAT 26 and BAT 36 as well as the BAT-AEPL set out under BAT 54.

This technique is especially suitable to oil refining sites:

- with a recognised site complexity, multiplicity of combustion and process units interlinked in terms of their feedstock and energy supply;
- with frequent process adjustments required in function of the quality of the crude received;
- with a technical necessity to use a part of process residues as internal fuels, causing frequent adjustments of the fuel mix according to process requirements.

BAT-associated emission levels: See Table 5.19.

In addition, for each new combustion unit, new FCC unit or new waste gas sulphur recovery unit included in the integrated emission management system, the BAT-AELs set out under BAT 26 and BAT 36 and the BAT-AEPL set out under BAT 54 remain applicable.

Table 5.19: BAT-associated emission levels for SO₂ emissions to air when applying BAT 58

The BAT-AEL for SO₂ emissions from the units concerned by BAT 58, expressed in mg/Nm³ as a monthly average value, is equal to or less than the weighted average of the SO₂ concentrations (expressed in mg/Nm³ as a monthly average) that would be achieved by applying in practice at each of those units techniques that would enable the units concerned to meet the following:

- (a) for catalytic cracking process (regenerator) units: the BAT-AEL ranges set out in Table 5.6 (BAT 26);
- (b) for combustion units burning refinery fuels alone or simultaneously with other fuels: the BAT-AEL ranges set out in Table 5.13 and in Table 5.14 (BAT 36); and
- (c) for waste gas sulphur recovery units: the BAT-AEPL ranges set out in Table 5.17 (BAT 54).

This BAT-AEL is expressed by the following formula:

$$\frac{\Sigma[(\text{flue gas flow rate of the unit concerned}) \times (\text{SO}_2 \text{ concentration that would be achieved for that unit})]}{\Sigma (\text{flue gas flow rate of all units concerned})}$$

Notes:

1. The applicable reference conditions for oxygen are those specified in Table 5.1.
2. The weighing of the emission levels of the individual units is done on the basis of the flue-gas flow rate of the unit concerned, expressed as a monthly average value (Nm³/hour), which is representative for the normal operation of that unit within the refinery installation (applying the reference conditions under Note 1).
3. In case of substantial and structural fuel changes which are affecting the applicable BAT-AEL for a unit or other substantial and structural changes in the nature or functioning of the units concerned, or in case of their replacement, extension or the addition of combustion, FCC, or waste gas sulphur recovery units, the BAT-AEL defined in Table 5.19 needs to be adjusted accordingly.

Monitoring associated with BAT 58

BAT for monitoring emissions of SO₂ under an integrated emission management technique is as in BAT 4, complemented with the following:

- a monitoring plan including a description of the processes monitored, a list of the emission sources and source streams (products, waste gases) monitored for each process and a description of the methodology (calculations, measurements) used and the underlying assumptions and associated level of confidence;
- continuous monitoring of the flue-gas flow rates of the units concerned, either through direct measurement or by an equivalent method;
- a data management system for collecting, processing and reporting all monitoring data needed to determine the emissions from the sources covered by the integrated emission management technique.

GLOSSARY

5.20 Description of techniques for the prevention and control of emissions to air

5.20.1 Dust

| Technique | Description |
|----------------------------------|---|
| Electrostatic precipitator (ESP) | Electrostatic precipitators operate such that particles are charged and separated under the influence of an electrical field. Electrostatic precipitators are capable of operating under a wide range of conditions. Abatement efficiency may depend on the number of fields, residence time (size), catalyst properties and upstream particles removal devices. At FCC units, 3-field ESPs and 4-field ESPs are commonly used. ESPs may be used on a dry mode or with ammonia injection to improve the particle collection. For the calcining of green coke, the ESP capture efficiency may be reduced due to the difficulty for coke particles to be electrically charged |
| Multistage cyclone separators | Cyclonic collection device or system installed following the two stages of cyclones. Generally known as a third stage separator, common configuration consists of a single vessel containing many conventional cyclones or improved swirl-tube technology. For FCC, performance mainly depends on the particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones |
| Centrifugal washers | Centrifugal washers combine the cyclone principle and an intensive contact with water e.g. venturi washer |
| Third stage blowback filter | Reverse flow (blowback) ceramic or sintered metal filters where, after retention at the surface as a cake, the solids are dislodged by initiating a reverse flow. The dislodged solids are then purged from the filter system |

5.20.2 Nitrogen oxides (NO_x)

| Technique | Description |
|---|--|
| Combustion modifications | |
| Staged combustion | <ul style="list-style-type: none"> Air staging – involves substoichiometric firing in a first step and the subsequent addition of the remaining air or oxygen into the furnace to complete combustion Fuel staging – a low impulse primary flame is developed in the port neck; a secondary flame covers the root of the primary flame reducing its core temperature |
| Flue-gas recirculation | Reinjection of waste gas from the furnace into the flame to reduce the oxygen content and therefore the temperature of the flame. Special burners using the internal recirculation of combustion gases to cool the root of the flames and reduce the oxygen content in the hottest part of the flames |
| Use of low-NO _x burners (LNB) | The technique (including ultra-low-NO _x burners) is based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber. The design of ultra-low-NO _x burners (ULNB) includes combustion staging (air/fuel) and flue-gas recirculation. Dry low-NO _x burners (DLNB) are used for gas turbines |
| Optimisation of combustion | Based on permanent monitoring of appropriate combustion parameters (e.g. O ₂ , CO content, fuel to air (or oxygen) ratio, unburnt components), the technique uses control technology for achieving the best combustion conditions |
| Diluent injection | Inert diluents, e.g. flue-gas, steam, water, nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NO _x in the flue-gases |
| Selective catalytic reduction (SCR) | The technique is based on the reduction of NO _x to nitrogen in a catalytic bed by reaction with ammonia (in general aqueous solution) at an optimum operating temperature of around 300 – 450 °C. One or two layers of catalyst may be applied. A higher NO _x reduction is achieved with the use of higher amounts of catalyst (two layers) |
| Selective non-catalytic reduction (SNCR) | The technique is based on the reduction of NO _x to nitrogen by reaction with ammonia or urea at a high temperature. The operating temperature window must be maintained between 900 °C and 1 050 °C for optimal reaction |
| Low temperature NO _x oxidation | The low temperature oxidation process injects ozone into a flue-gas stream at optimal temperatures below 150 °C, to oxidise insoluble NO and NO ₂ to highly soluble N ₂ O ₅ . The N ₂ O ₅ is removed in a wet scrubber by forming dilute nitric acid waste water that can be used in plant processes or neutralised for release and may need additional nitrogen removal |

5.20.3 Sulphur oxides (SO_x)

| Technique | Description |
|--|--|
| Treatment of refinery fuel gas (RFG) | Some refinery fuel gases may be sulphur-free at source (e.g. from catalytic reforming and isomerisation processes) but most other processes produce sulphur-containing gases (e.g. off-gases from the visbreaker, hydrotreater or catalytic cracking units). These gas streams require an appropriate treatment for gas desulphurisation (e.g. by acid gas removal — see below — to remove H ₂ S) before being released to the refinery fuel gas system |
| Refinery fuel oil (RFO) desulphurisation by hydrotreatment | In addition to selection of low-sulphur crude, fuel desulphurisation is achieved by the hydrotreatment process (see below) where hydrogenation reactions take place and lead to a reduction in sulphur content |
| Use of gas to replace liquid fuel | Decrease the use of liquid refinery fuel (generally heavy fuel oil containing sulphur, nitrogen, metals, etc.) by replacing it with on-site Liquefied Petroleum Gas (LPG) or refinery fuel gas (RFG) or by externally supplied gaseous fuel (e.g. natural gas) with a low level of sulphur and other undesirable substances. At the individual combustion unit level, under multi-fuel firing, a minimum level of liquid firing is necessary to ensure flame stability |
| Use of SO _x reducing catalysts additives | Use of a substance (e.g. metallic oxides catalyst) that transfers the sulphur associated with coke from the regenerator back to the reactor. It operates most efficiently in full combustion mode rather than in deep partial-combustion mode. NB: SO _x reducing catalysts additives might have a detrimental effect on dust emissions by increasing catalyst losses due to attrition, and on NO _x emissions by participating in CO promotion, together with the oxidation of SO ₂ to SO ₃ |
| Hydrotreatment | Based on hydrogenation reactions, hydrotreatment aims mainly at producing low-sulphur fuels (e.g. 10 ppm gasoline and diesel) and optimising the process configuration (heavy residue conversion and middle distillate production). It reduces sulphur, nitrogen and metal content of the feed. As hydrogen is required, sufficient production capacity is needed. As the technique transfer sulphur from the feed to hydrogen sulphide (H ₂ S) in the process gas, treatment capacity (e.g. amine and Claus units) is also a possible bottleneck |
| Acid gas removal e.g. by amine treating | Separation of acid gas (mainly hydrogen sulphide) from the fuel gases by dissolving it in a chemical solvent (absorption). The commonly used solvents are amines. This is generally the first step treatment needed before elemental sulphur can be recovered in the SRU |
| Sulphur recovery unit (SRU) | Specific unit that generally consists of a Claus process for sulphur removal of hydrogen sulphide (H ₂ S)-rich gas streams from amine treating units and sour water strippers. SRU is generally followed by a tail gas treatment unit (TGTU) for remaining H ₂ S removal |
| Tail gas treatment unit (TGTU) | A family of techniques, additional to the SRU in order to enhance the removal of sulphur compounds. They can be divided into four categories according to the principles applied: <ul style="list-style-type: none"> • direct oxidation to sulphur • continuation of the Claus reaction (sub-dewpoint conditions) • oxidation to SO₂ and recovering sulphur from SO₂ • reduction to H₂S and recovery of sulphur from this H₂S (e.g. amine process) |

| Technique | Description |
|----------------------------|--|
| Wet scrubbing | <p>In the wet scrubbing process, gaseous compounds are dissolved in a suitable liquid (water or alkaline solution). Simultaneous removal of solid and gaseous compounds may be achieved. Downstream of the wet scrubber, the flue-gases are saturated with water and a separation of the droplets is required before discharging the flue-gases. The resulting liquid has to be treated by a waste water process and the insoluble matter is collected by sedimentation or filtration</p> <p>According to the type of scrubbing solution, it can be:</p> <ul style="list-style-type: none"> • a non-regenerative technique (e.g. sodium or magnesium-based) • a regenerative technique (e.g. amine or soda solution) <p>According to the contact method, the various techniques may require e.g.:</p> <ul style="list-style-type: none"> • Venturi using the energy from inlet gas by spraying it with the liquid • packed towers, plate towers, spray chambers. <p>Where scrubbers are mainly intended for SO_x removal, a suitable design is needed to also efficiently remove dust.</p> <p>The typical indicative SO_x removal efficiency is in the range 85 – 98 %</p> |
| Non-regenerative scrubbing | <p>Sodium or magnesium-based solution is used as alkaline reagent to absorb SO_x generally as sulphates. Techniques are based on e.g.:</p> <ul style="list-style-type: none"> • wet limestone • aqueous ammonia • seawater (see infra) |
| Seawater scrubbing | <p>A specific non-regenerative type of scrubbing using alkalinity of the seawater as solvent. Generally requires an upstream abatement of dust</p> |
| Regenerative scrubbing | <p>Use of specific SO_x absorbing reagent (e.g. absorbing solution) that generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused</p> |

5.20.4 Combined techniques (SO_x, NO_x, and dust)

| Technique | Description |
|-------------------------------------|---|
| Wet scrubbing | See Section 5.20.3 |
| SNO _x combined technique | <p>Combined technique to remove SO_x, NO_x and dust where a first dust removal stage (ESP) takes place followed by some specific catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NO_x is reduced to N₂.</p> <p>Overall SO_x removal is in the range: 94 – 96.6 %.</p> <p>Overall NO_x removal is in the range: 87 – 90 %</p> |

5.20.5 Carbon monoxide (CO)

| Technique | Description |
|---|---|
| Combustion operation control | <p>The increase in CO emissions due to the application of combustion modifications (primary techniques) for the reduction of NO_x emissions can be limited by a careful control of the operational parameters</p> |
| Catalysts with carbon monoxide (CO) oxidation promoters | <p>Use of a substance which selectively promotes the oxidation of CO into CO₂ (combustion)</p> |
| Carbon monoxide (CO) boiler | <p>Specific post-combustion device where CO present in the flue-gas is consumed downstream of the catalyst regenerator to recover the energy</p> <p>It is usually used only with partial-combustion FCC units</p> |

5.20.6 Volatile organic compounds (VOC)

| Technique | Description |
|--------------------|---|
| Vapour recovery | <p>Volatile organic compounds emissions from loading and unloading operations of most volatile products, especially crude oil and lighter products, can be abated by various techniques e.g.:</p> <ul style="list-style-type: none"> • Absorption: the vapour molecules dissolve in a suitable absorption liquid (e.g. glycols or mineral oil fractions such as kerosene or reformat). The loaded scrubbing solution is desorbed by reheating in a further step. The desorbed gases must either be condensed, further processed, and incinerated or re-absorbed in an appropriate stream (e.g. of the product being recovered) • Adsorption: the vapour molecules are retained by activate sites on the surface of adsorbent solid materials, e.g. activated carbon (AC) or zeolite. The adsorbent is periodically regenerated. The resulting desorbate is then absorbed in a circulating stream of the product being recovered in a downstream wash column. Residual gas from wash column is sent to further treatment • Membrane gas separation: the vapour molecules are processed through selective membranes to separate the vapour/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate). • Two-stage refrigeration/condensation: by cooling of the vapour/gas mixture the vapour molecules condense and are separated as a liquid. As the humidity leads to the icing-up of the heat exchanger, a two stage condensation process providing for alternate operation is required. • Hybrid systems: combinations of available techniques <p><i>NB</i> Absorption and adsorption processes cannot notably reduce methane emissions.</p> |
| Vapour destruction | <p>Destruction of VOCs can be achieved through e.g. thermal oxidation (incineration) or catalytic oxidation when recovery is not easily feasible. Safety requirements (e.g. flame arrestors) are needed to prevent explosion. Thermal oxidation occurs typically in single chamber, refractory-lined oxidisers equipped with gas burner and a stack. If gasoline is present, heat exchanger efficiency is limited and preheat temperatures are maintained below 180 °C to reduce ignition risk. Operating temperatures range from 760 °C to 870 °C and residence times are typically 1 second. When a specific incinerator is not available for this purpose, an existing furnace may be used to provide the required temperature and residence times. Catalytic oxidation requires a catalyst to accelerate the rate of oxidation by adsorbing the oxygen and the VOCs on its surface. The catalyst enables the oxidation reaction to occur at lower temperature than required by thermal oxidation: typically ranging from 320 °C to 540 °C. A first preheating step (electrically or with gas) takes place to reach a temperature necessary to initiate the VOCs catalytic oxidation. An oxidation step occurs when the air is passed through a bed of solid catalysts</p> |

| Technique | Description |
|--|--|
| LDAR (leak detection and repair) programme | <p>An LDAR (leak detection and repair) programme is a structured approach to reduce fugitive VOC emissions by detection and subsequent repair or replacement of leaking components. Currently, sniffing (described by EN 15446) and optical gas imaging methods are available for the identification of the leaks.</p> <p>Sniffing method: The first step is the detection using hand-held VOC analysers measuring the concentration adjacent to the equipment (e.g. by using flame ionisation or photo-ionisation). The second step consists of bagging the component to carry out a direct measurement at the source of emission. This second step is sometimes replaced by mathematical correlation curves derived from statistical results obtained from a large number of previous measurements made on similar components.</p> <p>Optical gas imaging methods: Optical imaging uses small lightweight hand-held cameras which enable the visualisation of gas leaks in real time, so that they appear as 'smoke' on a video recorder together with the normal image of the component concerned to easily and rapidly locate significant VOC leaks. Active systems produce an image with a back-scattered infrared laser light reflected on the component and its surroundings. Passive systems are based on the natural infrared radiation of the equipment and its surroundings</p> |
| VOC diffuse emissions monitoring | <p>Full screening and quantification of site emissions can be undertaken with an appropriate combination of complementary methods, e.g. Solar occultation flux (SOF) or differential absorption lidar (DIAL) campaigns. These results can be used for trend evaluation in time, cross checking and updating/validation of the ongoing LDAR programme.</p> <p>Solar occultation flux (SOF): The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband infrared or ultraviolet/visible sunlight spectrum along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes.</p> <p>Differential absorption LIDAR (DIAL): DIAL is a laser-based technique using differential adsorption LIDAR (light detection and ranging) which is the optical analogue of sonic radio wave-based RADAR. The technique relies on the back-scattering of laser beam pulses by atmospheric aerosols, and the analysis of spectral properties of the returned light collected with a telescope</p> |
| High-integrity equipment | <p>High-integrity equipment includes e.g.:</p> <ul style="list-style-type: none"> • valves with double packing seals • magnetically driven pumps/compressors/agitators • pumps/compressors/agitators fitted with mechanical seals instead of packing • high-integrity gaskets (such as spiral wound, ring joints) for critical applications |

5.20.7 Other techniques

| Technique | Description |
|--|---|
| Techniques to prevent or reduce emissions from flaring | <p>Correct plant design: includes sufficient flare gas recovery system capacity, the use of high-integrity relief valves and other measures to use flaring only as a safety system for other than normal operations (start-up, shutdown, emergency).</p> <p>Plant management: includes organisational and control measures to reduce flaring events by balancing RFG system, using advanced process control, etc.</p> <p>Flares design: includes height, pressure, assistance by steam, air or gas, type of flare tips, etc. It aims at enabling smokeless and reliable operations and ensuring an efficient combustion of excess gases when flaring from non-routine operations.</p> <p>Monitoring and reporting: Continuous monitoring (measurements of gas flow and estimations of other parameters) of gas sent to flaring and associated parameters of combustion (e.g. flow gas mixture and heat content, ratio of assistance, velocity, purge gas flow rate, pollutant emissions). Reporting of flaring events makes it possible to use flaring ratio as a requirement included in the EMS and to prevent future events. Visual remote monitoring of the flare can also be carried out by using colour TV monitors during flare events</p> |
| Choice of the catalyst promoter to avoid dioxins formation | <p>During the regeneration of the reformer catalyst, organic chloride is generally needed for effective reforming catalyst performance (to re-establish the proper chloride balance in the catalyst and to assure the correct dispersion of the metals). The choice of the appropriate chlorinated compound will have an influence on the possibility of emissions of dioxins and furans</p> |
| Solvent recovery for base oil production processes | <p>The solvent recovery unit consists of a distillation step where the solvents are recovered from the oil stream and a stripping step (with steam or an inert gas) in a fractionator.</p> <p>The solvents used may be a mixture (DiMe) of 1,2-dichloroethane (DCE) and dichloromethane (DCM).</p> <p>In wax-processing units, solvent recovery (e.g. for DCE) is carried out using two systems: one for the deoiled wax and another one for the soft wax. Both consist of heat-integrated flashdrums and a vacuum stripper. Streams from the dewaxed oil and waxes product are stripped for removal of traces of solvents</p> |

5.21 Description of techniques for the prevention and control of emissions to water

5.21.1 Waste water pretreatment

| Technique | Description |
|--|---|
| Pretreatment of sour water streams before reuse or treatment | Send generated sour water (e.g. from distillation, cracking, coking units) to appropriate pretreatment (e.g. stripper unit) |
| Pretreatment of other waste water streams prior to treatment | To maintain treatment performance, appropriate pretreatment may be required |

5.21.2 Waste water treatment

| Technique | Description |
|---|---|
| Removal of insoluble substances by recovering oil. | <p>These techniques generally include::</p> <ul style="list-style-type: none"> • API Separators (APIs) • Corrugated Plate Interceptors (CPIs) • Parallel Plate Interceptors (PPIs) • Tilted Plate Interceptors (TPIs) • Buffer and/or equalisation tanks |
| Removal of insoluble substances by recovering suspended solid and dispersed oil | <p>These techniques generally include:</p> <ul style="list-style-type: none"> • Dissolved Gas Flotation (DGF) • Induced Gas Flotation (IGF) • Sand Filtration |
| Removal of soluble substances including biological treatment and clarification | <p>Biological treatment techniques may include:</p> <ul style="list-style-type: none"> • Fixed bed systems • Suspended bed systems. <p>One of the most commonly used suspended bed system in refineries WWTP is the activated sludge process. Fixed bed systems may include a biofilter or trickling filter</p> |
| Additional treatment step | A specific waste water treatment intended to complement the previous treatment steps e.g. for further reducing nitrogen or carbon compounds. Generally used where specific local requirements for water preservation exist. |

6 EMERGING TECHNIQUES

Emerging technique is understood in this document as a novel technique that has not yet been applied in any industrial sector on a commercial basis. This chapter contains these techniques that may appear in the near future and that may be applicable to the refinery sector.

6.1 Refinery activities overview

Throughout its history the refining industry has continuously developed new and improved processes in response to changes in feed quality, product specifications, product slates, new product outlets and economic and environmental requirements. These developments have slowed down in recent years for the following reasons.

- Large oil companies are cutting down on their R&D budgets, and are increasingly relying on third parties for new developments in refinery technology and catalytic processes. These third parties develop techniques for licensing income or for income from catalyst sales. Developments are reported in the technical literature (Hydrocarbon Processing, Chemical Engineering Progress, Oil and Gas Journal, Erdöl, Gas und Kohle, Petroleum Technology Review) and during seminars and conferences (World Petroleum Congress, WEFA, Hart's Fuel Conference, European Refining Technology Conference, NPRA and API specialist meetings) for the dissemination of these techniques.
- Technological developments are concentrating on optimising current systems for higher yields (e.g. more selective catalysts and solvents), higher energy efficiency (e.g. improved reactor design and better heat integration) and shorter downtimes (e.g. scavenging of impurities, automatic cleaning systems), rather than on novel processes.
- The current toolbox of conversion, separation, treatment and environmental technologies seems adequate and sufficient to meet any desired product slate and product specifications for the coming decade, as well as meeting stringent regulatory requirements.

Meanwhile, the upgrading process of the refinery sector to implement existing techniques for meeting new product specifications will continue. The rationalisation process in the refining industry also continues and low margins are forcing refineries to look for cost savings.

6.2 Alkylation

6.2.1 Alkylation of paraffins

As described in Chapter 2, there are four routes being pursued for development of alkylation:

- sulphuric acid;
- hydrofluoric acid;
- solid-acid;
- ionic liquids.

6.2.1.1 Sulphuric acid process

This is the most commonly used alkylation process but it has not seen dramatic improvements in recent years.

6.2.1.2 Hydrofluoric acid (HF) process

The HF route has experienced upgrades aiming to reduce hazardous problems (see Chapter 2).

6.2.1.3 Solid-acid technology

There have been substantial achievements in the following options during recent years and these processes have now become commercially available.

- In the Alkyclean process (Lummus/Albemarle), simultaneous reactors carry out a mild liquid phase regeneration and periodically a reactor undergoes a higher temperature vapour phase H₂ strip. No generation of acid-soluble oils occurs.
- UOP Alkylene is based on increasing the density of catalyst acid sites and achieving a high reactivation degree. Impurities in the feedstock do not need treatment. One contract has been awarded in Azerbaijan.
- Exelus Exsact is based on keeping the catalyst stable for up to 24 hours, with periodic catalyst reactivation.
- Other initiatives are ongoing and some have reached commercialisation (e.g. Fixed Bed of super acid catalyst in solid support by Haldor Topsoe; acid Chevron Isoalky, Eurofuel from Lurgi.).

In the AlkyClean solid-acid process, the reactors operate in the liquid phase at 50 – 90 °C at about 21 barg. No chilling is required in this process. The general process scheme (see Figure 6.1 and Figure 6.2) is similar to that used in the case of HF and H₂SO₄ liquid acid alkylation processes. The main difference is the use of a solid-acid catalyst, which does not contain any volatile components. Isobutane is recycled through a set of reactors that contain a fixed bed catalyst. Olefins are injected in such a way that the olefin is well dispersed in order to keep the olefin concentration low. No corrosive and poisonous liquid acid catalysts are used. The fixed bed catalyst has a lifetime of several years and therefore catalyst consumption is low, compared to liquid technologies. Furthermore no acid-soluble oil waste is formed and no downstream treatment is required to remove traces of liquid acids or halogen compounds from the product. The products contain no nitrogen, sulphur (H₂SO₄ process) or halogens (HF process).

Overall olefin conversion is almost 100 % and the yield and quality of the product are similar to that found with the liquid acid processes. Regeneration of the catalyst is carried out

continuously by cyclic switching from olefins addition to the addition of a small amount of dissolved hydrogen without changing the reactor conditions.

Depending on the severity of operation, the overall conversion of olefins will drop slowly below 99 – 99.5 % after some time. Moderate temperature (about 250 °C) regeneration with hydrogen gas is carried out for the complete catalyst activity and selectivity.

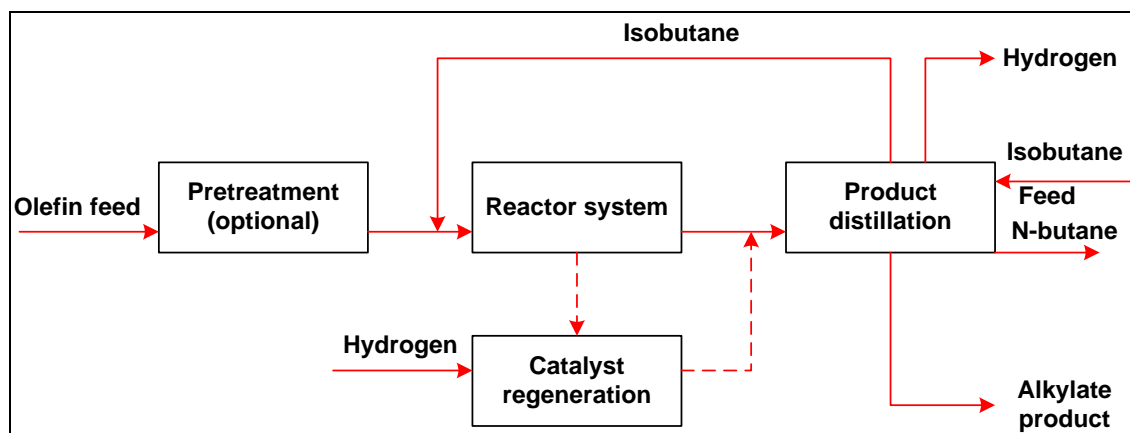


Figure 6.1: Simplified block diagram of the AlkyClean solid-acid alkylation process

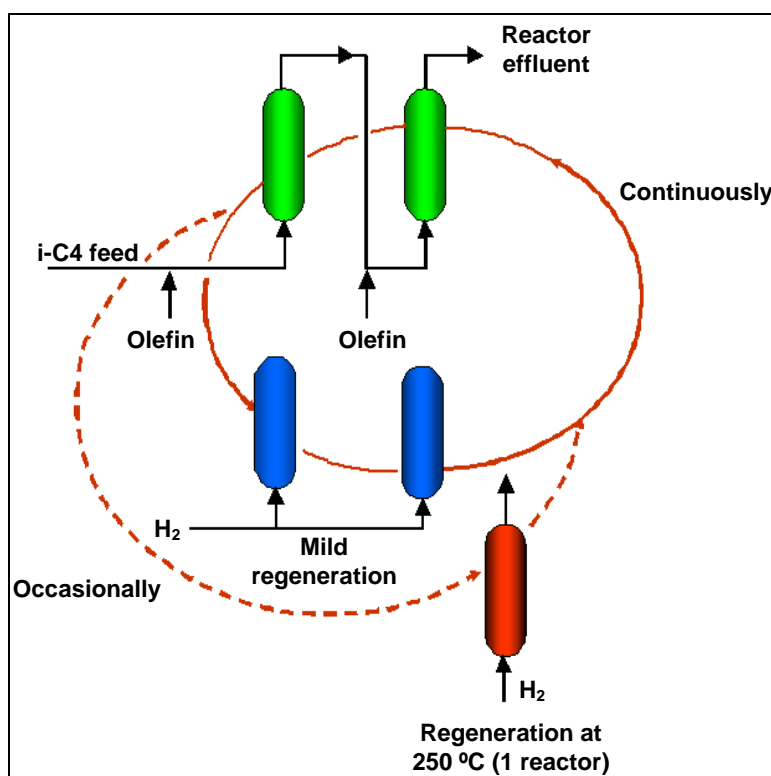


Figure 6.2: Simplified reaction/regeneration scheme of the AlkyClean solid-acid alkylation process

Achieved environmental benefits

The main advantage of the solid-acid alkylation process is the fact that no liquid acids are needed. As a consequence catalyst consumption is the lowest of all the processes. The *in situ* regeneration of the catalyst with hydrogen creates a product gas that can be reused in other applications of the refinery, since it contains no acids or halogens. No routine flaring of gas is required. Also, no waste water or sludge is produced from the acid neutralisation units.

Furthermore, the absence of liquid acids or any halogens will mean that no product treatment or disposal of acids is needed. There will be no acid-soluble oil produced in a solid-acid alkylation unit.

No corrosive or erosive environment is expected in this alkylation process, so on-stream reliability is expected to be high and maintenance low compared to HF and sulphuric processes. This reduces the chance of accidental emissions of hydrocarbons (and acids in the case of HF and H₂SO₄).

Cross-media effects

Effluent gas emissions

Gas effluent from regeneration can be used as a diluted hydrogen source or in the refinery fuel gas system. Fugitive emissions contain only hydrocarbons and no acids or acid components. Furthermore, since no corrosive environment is created in the case of solid-acid alkylation, maintenance and repairs are expected to be lower. This will reduce the overall fugitive emission levels of hydrocarbons considerably, compared to liquid acid technologies.

Effluent liquid discharges

None.

Waste elimination

No tars are produced. Only spent catalyst will, after many years of operation, be a solid waste. The catalyst is a fixed bed catalyst that contains zeolite, alumina and a very low concentration of noble metal. Consequently, it is relatively harmless and can easily be transported for the off-site reclaiming of noble metal. The noble metal is reutilised, while the solids can be reused in the building industry. The amount of spent catalyst produced by the AlkyClean solid-acid alkylation process is about a factor 100 lower than HF alkylation, and a factor 1 000 lower than sulphuric alkylation.

Operational data

There are no liquid acids or halogens so there are no corrosion issues. Based on a demonstration plant, the maintenance costs for equipment are expected to be much lower than in the case of the liquid acid processes.

No special safety precautions are required, other than those for any refinery unit processing hydrocarbons.

There is no need for expensive mitigation (acid dump and water spray systems) and vapour pressure suppression facilities, such as those that are required for HF units. Compared to H₂SO₄ units, catalyst consumption is lower and does not require large daily transports of spent and regenerated acid to external regeneration facilities.

Applicability

The retrofit of conventional HF or H₂SO₄ units with a solid-acid process is impossible. AlkyClean utilises a swing reactor system, which makes an on-stream catalyst change out of the catalyst possible and thus turnarounds can be tailored to fit the refinery's schedule. In the case of repairs involving one of the reactors, the unit can remain on-stream using the remaining reactors. In addition, it is to be noted that cycling the reactors frequently between reaction and regeneration may lead to additional costs, operating complexity and reliability challenges.

Economics

For solid-acid alkylation, utility and chemical costs will be somewhat higher than reported in the case of hydrofluoric alkylation, but lower than those of the H₂SO₄ process, since the AlkyClean process has much lower catalyst consumption. Table 6.1 shows the data resulting from a US project evaluation in 2008. See also Sections 4.2.1 and 4.2.2.

Table 6.1: Utility and chemical costs of the three alkylation processes

| Values per tonne of alkylate produced | Sulphuric acid | Hydrofluoric | Solid acid |
|---|-----------------------------|---------------------|----------------------|
| Utilities | | | |
| Electricity (USD 0.06/kWh) | 7.7 | 1.20 – 3.90 | 8.02 |
| Fuel (USD 0.006/MJ) | No | 5.7 – 17.06 | No |
| Steam (USD 0.014/kg) | 11.71 | 1.41 – 14.11 | 14.50 |
| Cooling water (USD 0.026/m ³) | 1.90 | 1.64 | 0.02 |
| Industrial water | negligible | negligible | negligible |
| Chemicals | | | |
| Fresh acid (kg) | 25.74 – 39.6 ⁽²⁾ | 1.64 | 13.48 ⁽¹⁾ |
| Caustic (USD 0.55/kg) | 0.23 | 0.31 | No |
| Total | 47.28 – 61.14 | 24.6 – 25.96 | 36.02 |
| ⁽¹⁾ Based on 2008 Pt price and used Pt lease rate 5 %. | | | |
| ⁽²⁾ Based on sulphuric acid price of USD 330/tonne. | | | |

The overall investment and operational costs for a new alkylation unit are projected to be significantly lower if choosing the solid-acid process instead of an HF unit, due to substantial savings on the safety devices required (e.g. leak detection, water spray systems, acid dump facilities) and safety management procedures and equipment to be implemented for HF units operation.

Driving force for implementation

Production of an excellent gasoline blending component with a high octane number and low sulphur, nitrogen, benzene and aromatics contents, by using a clean solid-acid catalyst technology that replaces corrosive and poisonous liquid acid technologies. This technique has the potential to provide a dramatic reduction of the environmental impact and risk to refinery employees and nearby communities. This technique was given the ‘Affordable Green Chemistry Award’ in 2010 from the American Chemical Society.

Example plants

No full-size commercial unit is in operation yet. However, the technology has been developed over a 10-year intensive research and development period, on a laboratory and pilot plant scale. During this period Albemarle started a project in cooperation with the engineering company Lummus Technology to check and improve the technology from an engineering point of view.

After the R&D period, the catalyst was produced on a full-size commercial plant scale to demonstrate that commercial production of the catalyst is possible. This resulted in a high-performance catalyst that was used to operate a demonstration AlkyClean alkylation plant at Neste Oil’s refinery in Porvoo (Finland).

Reference Literature

[52, Van Broekoven et al. 2008], [53, Van Rooijen et al.2009].

6.2.1.4 Ionic liquids (IL)

Ionikylation is an isobutane alkylation process. The process uses a composite-ionic liquid (IL) as homogeneous catalyst for alkylation reactions at ambient temperatures and moderate pressures. ILs are ionic, salt-like materials that are liquid at less than 100 °C. ILs have historically been used as solvents and homogeneous catalysts due to their negligible vapour pressure, good solubility to a wide range of organic and inorganic compounds, and ability to be recycled for reuse. Acidic chloroaluminate (III) IL has been used as a homogeneous catalyst for isobutane alkylation. Its use eliminates the diffusion limitation present with solid-acid catalyst systems, and alkylated gasoline is more easily separated from the ionic liquid.

Active components in alkylate gasoline are iso-octane or trimethylpentanes (TMPs). Nevertheless, TMP yield and selectivity are low with conventional IL, with and without adjusting the IL's acidity by varying either the molar fraction of aluminium chloride (AlCl_3) of the IL or adding hydrochloric acid (HCl). A study showed that adding aromatic hydrocarbons and metal chlorides to aluminium chloride-dialkyl ether complex enhanced the TMP selectivity.

A pilot plant exists in China (retrofitted into an existing 65 000 t/yr sulphuric acid plant).

Source: [88, Oil & Gas Journal, ZC et al. 2006]

6.2.2 Alkylation aiming to reduce benzene content in gasoline

See Section 6.14 on product treatments.

6.3 Base oil production

A new technology is the application of membranes for solvent recovery in solvent extraction/dewaxing processes. The driving force is the reduction in energy consumption. [202, Dekkers 2000]

6.4 Catalytic cracking

Some promising lines of investigation for the improvement of the environmental performance of catalytic cracking units are:

- The capability to process heavier feedstocks, containing more contaminants (catalyst deactivators) such as vanadium and nickel and having a higher Conradson Carbon Residue (CCR) content. Responses that are being developed are: to continue the development of more active catalysts and more effective (e.g. two-stage) catalyst regeneration. Driving forces are the reduction of residue (i.e. enhanced upgrading) and higher overall refinery efficiency (e.g. the elimination of high vacuum unit operation) [202, Dekkers 2000].
- Improvement of the catalyst separation by use of a magnet (Kellogg Tech company). [191, UBA Austria 1998]

6.5 Catalytic reforming

The current practice of applying continuously improved catalysts (supplied by catalyst manufacturers) is expected to continue. [202, Dekkers 2000]

6.6 Coking

Total coke gasification is regarded as the key future technology for deep desulphurisation and hydrogen production. In this process, crude oil can be refined without the co-production of heavy oil residues.

The interest (research papers and other publications) and investment in the potential refinery use of coke for energy purposes is growing. IGCC and CFB Boiler technologies are being further developed, optimised and applied with the use of coke feedstock.

6.7 Energy system

Some promising lines of investigation for the improvement of the environmental performance of the energy systems are CO₂ abatement techniques (more information in Section 6.15 on Waste gas treatments). Another is the heat integration. The search for further energy improvements is continuing, with the current focus on attractive cogeneration opportunities and more complex heat integration.

6.8 Etherification

Methanol to gasoline (MTG) reactions dehydrate methanol and convert the available carbon and hydrogen into various hydrocarbons.

The ‘Shape-Selective’ MTG catalyst limits the synthesis reactions to 10 carbons, which results in a sulphur-free gasoline with a typical 92 Research Octane Number (RON).

The first MTG plant (14 500 barrels per day capacity) was operated at Plymouth (New Zealand) from 1985 to 1997, converting natural gas to gasoline.

A second generation MTG plant has started in China (Shanxi province).

Source: [114, ExxonMobil Research and Engineering 2013]

6.9 Hydrogen production

Some promising lines of investigation in hydrogen production technologies are:

- The hydrocarb process, in which the residual oil is essentially cracked to carbon and hydrogen. This process can be seen as an internal source of natural gas for a refinery. The process produces carbon, hydrogen and methanol. It has been calculated in a refinery of 4.98 Mt/yr that this process can increase the total gasoline production by 40 %, i.e. to 1 150 m³/d of methanol and 795 m³/d of C/H₂O slurry [78, Steinberg et al. 1992].
- Methane pyrolysis, which takes advantage of the thermal decomposition of natural gas and the direct production of hydrogen while sequestering the carbon or using the carbon for other commodity purposes. Consequently, the CO₂ generation is completely eliminated [78, Steinberg et al. 1992], [213, Steinberg 2000].

Some hydrogen purification process developments enable lower costs by using new techniques such as structured adsorbent beds and integrated rotary valves. The rapid cycle pressure swing adsorption (RCPSA) process claims to enable:

- cheaper construction costs (30 % to 50 %) compared to PSA and low operating costs;
- smaller plot space requirement - as little as one quarter of PSA.

Source: [281, Exxon Mobil Research and Engineering 2010]

6.10 Hydrogen-consuming processes

Some promising lines of investigation for the improvement of the environmental performance of energy systems are:

- Residue hydrotreating and hydroconversion processes (e.g. slurry bed technology). These processes have only been demonstrated at a semi-commercial scale and no commercial plants are in operation yet.
- Gasoline deep desulphurisation techniques with a lower hydrogen consumption are currently under development. Parameters are not yet available.

Also, it is to be noted that bunker fuel oil desulphurisation is one of the next technical challenges ahead that could possibly lead to new techniques or significant improvements in the current ones.

Deep gasoline and gas oil desulphurisation

These process have gained importance during recent years. Many of the new design improvements, optimisation or new grass roots processes are now reaching the commercialisation stage.

- In the standard HDS process now operated under more severe conditions, there are a large number of new generation catalysts that are more active and more selective. These lead to a direct impact on the overall process efficiency.
- New process developments use less H₂-consuming technologies. Reactive adsorption at high temperature using metal oxide sorbent or alumina-based adsorption are delivering promising results. Selective extraction or polar adsorption (Irvad process) are also emerging techniques to consider.

Non-H₂ desulphurisation techniques

Oxidative desulphurisation may be one of the most promising in this group (see Section 2.13), but there are still some design challenges to overcome.

Below is a list of some other emerging techniques:

- olefin alkylation of thiophenic sulphur (OATS process by BP);
- polymer membrane (S-Brane technique by Grace);
- caustic extraction (Exomer process by Exxon);
- biochemical desulphurisation (Energy biosystems);
- selective adsorption (Penn State SARS).

Source: 'Recent advances in the science and technology of ultra low sulphur diesel (ULSD) production'. [80, Stanislaus et al.2010]

Selective desulphurisation of the main unit feedstock

Treating the primary distillation outlet stream is becoming more common.

Feedstock purification before further use in a refining process includes for example:

- C₃ or C₄ olefinic cut from FCC: alkynes and diolefins selective hydrogenation before further use in an alkylation or oligomerisation process; naphtha from visbreaking, coking: diolefins and olefins selective hydrogenation before further use in the catalytic reforming process;
- feedstock purification to obtain on-spec products, for example steam-cracked gasoline: selective hydrogenation of dienes is mandatory in order to stabilise the gasoline without octane loss;

- feedstock purification to produce petrochemical intermediates, for example a C2 olefinic cut from steam cracking: selective acetylene hydrogenation in order to produce on-spec ethylene without ethylene yield loss.

6.11 Hydrocracking

The treatment of heavier feedstocks requires optimal technical solutions that include catalyst and flow scheme considerations. Hydrotreatment is done before the cracking step.

- Once-through (85 – 90 %) conversion is done with minimal investment. Delivers middle distillates and high residue value.
- Single-stage full conversion requires medium investment but a higher product quality is achieved. Higher middle distillates selectivity is also achieved.
- Two-stage full conversion requires the highest investment costs. This scheme delivers the highest quality and best diesel/kerosene ratio (IFP and UOP developments).

6.12 Isomerisation

Catalytic hydro-isomerisation of long paraffins to produce biofuels

This technique uses the selectivity of the zeolites to improve the conversion of n-paraffins.

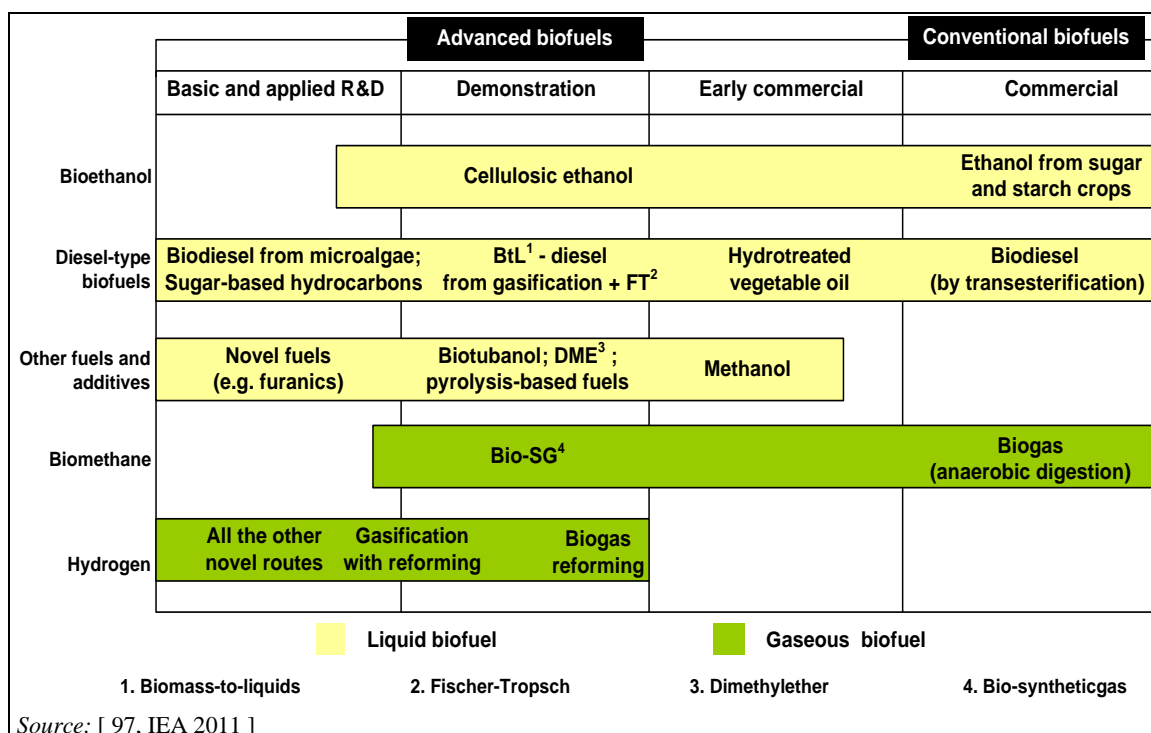


Figure 6.3: Status of main biofuels technologies

The biogas oils are produced from mainly triglyceride-containing feedstocks (vegetable oils, used frying oils, animal fats, etc.) by heterogenic catalytic hydrogenation in one or more stages. They contain mainly normal paraffins which are undesirable due for example to the freezing points of the C16 – C18 normal paraffins being between +18 °C and +28 °C. For this reason, it is needed to convert the chemical structure of the n-paraffins into isoparaffins having lower freezing points and still high cetane number.

Isomerisation dewaxing (Mobil MIDW) is applied to various streams (renewable diesel dewaxing) and is based on catalyst shape selectivity, including a zeolite and a metal for dehydrogenation/hydrogenation. Selectively converts long chain paraffins to isoparaffins.

This enables fuels to flow at low temperatures. This technique is currently in operation in eight units.

6.13 Primary distillation

Among developments to reduce the energy consumption by primary distillation in refineries, the divided wall column technique is to be distinguished.

Divided wall column

A DWC is a distillation column that has a vertical partition wall in the central section.

- The column may contain either trays or packing.
- The feed side of the two compartments acts as the prefractionator and the product side as the main column.
- In the case of a sharp split, a DWC can be used to produce three pure products from a single tower.
- A DWC can handle more than three components.

A DWC can typically cut capital and energy costs by approximately 30 % compared to a traditional two-column system.

6.14 Product treatments

*Bio*desulphurisation of gas oil and even crude oil: still under development.

[202, Dekkers 2000]

Reforming gasoline accounts for 70 – 85 % of the benzene presented in the gasoline pool (US EPA).

Pretreatment technologies that withdraw benzene precursors from the reforming feedstock are currently facing some difficulties: e.g. octane and hydrogen forming reduction, and difficulties to comply with benzene specifications. Removing benzene precursors from the reformer feed nearly eliminates (0.3 % w/w) benzene in the reformat. By using a dehexaniser with a side column, the top composition remains unchanged.

Post-treatment technologies:

- Benzene saturation, converts benzene to cyclohexane, sometimes coupled with isomerisation to increase octane. Some of the saturation technology drawbacks are: hydrogen consumption, loss of octane number and benzene conversions that may not be sufficient to achieve the required level.
- Benzene extraction. Gasoline volume reductions, need for proprietary solvents that require a high level of heat, storage facilities and an available market for the extracted benzene are disadvantages of the extraction technology. Expensive.
- Benzene alkylation, offers increments in octane number and gasoline volume, although the technology is considered pioneer. It is the only benzene reduction option that increases the volume for gasoline and does not lead to the consumption of H₂.

6.15 Waste gas treatments

Some developments to be mentioned are:

- biological H₂S removal [4, *Hydrocarbon Processing* 1998];
- particulate abatement techniques by new developments including ceramic filters (e.g. NGK, Japan) and a rotating particulate separator (Lebon and Gimbrair, the Netherlands);
- CO₂ abatement techniques.

Emerging techniques to enable carbon dioxide capture and storage (CCS)

The production of power and other use of fossil energy are the largest source of greenhouse gas emissions. For many years, there has been considerable international interest in the development of technology for the capture and storage of CO₂, particularly from coal-fired power plants. The IPCC report points out that the technology for capture and storage of CO₂ is not yet mature.

With CCS, a power plant could reduce its CO₂ emissions to the atmosphere by approximately 80 – 90 % compared to a plant without CCS. At the same time, CCS leads to a loss in overall efficiency of power plants or industrial processes due to the additional energy required for capture, transport and storage. The additional energy required for CCS depends on intrinsic performances of the capture system and on the energy management in the global installation.

A power plant equipped with a CCS system would need roughly 10 – 40 % more energy than a plant of equivalent output without CCS, of which most is for capture and compression.

As an example, the range reflects three types of power plants: for Natural Gas Combined Cycle plants, the range is 11 – 22 %, for Pulverised Coal plants, 24 – 40 % and for Integrated Gasification Combined Cycle plants, 14 – 25 % (*Source: IPCC report*).

Technique for capturing CO₂

These techniques are still in the early stages of development and are being tested in pilot plants. The available technology is highly expensive, and there are many uncertainties linked to the costs and operation of a CO₂ chain. They can be divided into three main categories:

- post-combustion;
- precombustion;
- oxy-fuel.

Post-combustion entails separating CO₂ from the exhaust gas from the power plant using chemical absorption. Because CO₂ is separated from the exhaust gas, this technology can, in principle, be utilised in existing power plants without major modifications of the plant itself. Post-combustion is considered to be the most mature technology, although there is still uncertainty surrounding its use and a need for significant technology improvements before it can be operated on commercial terms and on a large scale.

With the aid of ***precombustion*** technology, CO₂ is captured before combustion. This is accomplished by converting the natural gas to a hydrogen-rich gas mixture. This gas mixture is treated so that CO₂ is captured, and the new fuel is thus ‘decarbonised’ (exhaust gas contains very little CO₂). Although precombustion capture requires modification of the gas turbines to burn hydrogen-rich gas streams, the preceding steps are technically proven in the form of ammonia production plants worldwide.

With ***oxy-fuel***, combustion takes place in the gas turbine with pure oxygen instead of air. This means that the exhaust contains water vapour and CO₂, and the CO₂ can be separated out by cooling the exhaust. Today’s gas turbines suffer from low performance with oxygen combustion, and to date there has been little effort to develop new types of turbines that are better suited to oxygen combustion. In addition, production of oxygen is energy-intensive, and

the corresponding technology is quite costly. Of the three categories of capture technologies, oxy-fuel is the least mature.

The costs associated with capturing CO₂ from a power plant amount to approximately two-thirds of the costs for the entire CO₂ chain, while transport and storage amount to approximately one-third.

Transport of CO₂

CO₂ must be transported from the CO₂ source to the geological structure where the CO₂ will be stored. This transport can be accomplished by pipeline or by ship. Transport is the least complicated element in the CO₂ chain, both as regards technology and the possibility of evaluating realistic costs. Anyhow, the transport of CO₂ requires substantial resources in terms of energy and costs. As CO₂ behaves very differently under various pressures and temperatures, transport must take place in a controlled manner to avoid the solid state and subsequent clogging of pipes or equipment. The choice of the means of transport will depend on the specific requirements, including the number of emission sources, the volume of emissions from each source, the distance from the source to the storage place and the volume of CO₂ to be transported. With existing technology, pipeline transport is believed to be the simplest and most cost-effective alternative.

Storage of CO₂

There is significant technical potential for storing CO₂ in geological formations around the world. Producing oil and gas fields, abandoned oil and gas fields, and other formations are all candidates for such storage. Storage in reservoirs that are no longer in operation is a good solution in terms of geology; because these structures are likely to be impermeable after having held oil and gas for millions of years. Other formations are also considered to be secure storage alternatives for CO₂.

Full-scale test in Norwegian refinery

At the Mongstad refinery, a new combined heat and power (CHP) plant with a capacity to produce 280 MW of electricity and 350 MW of heat came into operation in 2010. Within an agreement with Norway's government, a full-scale carbon capture facility is planned to be built at the Mongstad refinery. At the time of writing this document, a governmental decision with regard to the realisation of the project will be submitted by the end of 2016.

6.16 Waste water treatment

Emerging techniques on this issue are addressed in the CWW BREF [[6, COM 2003](#)].

7 CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

Timing of the review process

The key milestones of the review process are summarised in Table 7.1.

Table 7.1: Key milestones in the review of the BREF for the refining of mineral oil and gas

| Key milestone | Date |
|--|---------------------------|
| Reactivation of the TWG | 29 January 2008 |
| Call for wishes | 7 March 2008 |
| Kick-off meeting | 22 – 24 September 2008 |
| Subgroup discussions for elaborating the questionnaire | End of 2008 |
| Collection of information | April 2008 – January 2010 |
| First TWG subgroup meeting on the ‘bubble approach’ | May 2010 |
| First draft of revised REF BREF (D1) | 23 July 2010 |
| Second TWG subgroup meeting on the ‘bubble approach’ | April 2011 |
| Second draft of revised REF BREF (D2) | 16 March 2012 |
| Final TWG meeting | 11 – 15 March 2013 |

During the review process, a total of 19 refinery site visits were carried out, in 9 countries comprising mainly oil refineries of various sizes, configurations and levels of complexity, and also some gas refineries.

Sources of information and information gaps

A large number of documents were shared by the TWG to assist the review of the BREF for the Refining of Mineral Oil and Gas (REF BREF), principally via the Commission's BAT Information System (BATIS), thereby ensuring a high level of transparency.

Major contributions

Contributions included information on general aspects of the refining sector and also more specific information on refining units and particularly data emissions and techniques.

The data collection exercise provided a large basis for emissions data and techniques in use at the refinery site level: a total of 62 filled-in site-specific questionnaires were received by the European IPPC Bureau. In addition, during the commenting periods on the first and second draft of the revised REF BREF, complementary information, generally focusing on specific issues or process units, was provided. In particular, detailed information on emissions data was provided by CONCAWE (Industrial NGO) after the second draft. This information was shared via BATIS.

Information on specific issues discussed at the final TWG meeting

- Emissions to water of nitrogen compounds:
Based on the data from the refinery effluents, it was agreed that there is no need to monitor ammoniacal nitrogen, since the pH values are low enough and therefore will not lead to the formation of toxic compounds.
- Emissions to water of phenols:
It was agreed that the current data on phenols were misleading (data showing both phenol and phenol index results in the same table in Chapters 3 and 4) and that for the next review it is recommended to collect and use the data from monitoring of the phenol index instead of phenol.

Degree of consensus reached during the information exchange

A high degree of consensus was reached on the BAT conclusions. Nevertheless, some dissenting views were raised, as described in the following table.

Table 7.2: Split views

| Split view number | TWG member | Expression of the split view |
|-------------------|-----------------------------|--|
| 1 | AT, DE and EEB SE | A dissenting view was expressed by Austria, Germany and the European Environmental Bureau (EEB) who consider that BAT-associated emission levels (BAT-AELs) for emissions to water should refer, in general, to a short-term averaging period, i.e. daily average. A dissenting view was also expressed by Sweden proposing to express BAT-AELs for emissions to water as specific loads with the following levels: <ul style="list-style-type: none"> • COD: 10 – 50 g/t crude (yearly average); • Total Nitrogen: 2 – 15 g/t crude (yearly average). |
| 2 | AT, DE, NL and EEB | A dissenting view was expressed by Austria, Germany, the Netherlands and the European Environmental Bureau who considered that BAT-associated emission levels (BAT-AELs) for emissions to air should, in general, refer to a short-term averaging period, i.e. daily averages. |
| 4 | CONCAWE | A dissenting view was expressed by CONCAWE. This TWG member considers that the applicability restrictions should include economic considerations, e.g. by referring to 'high investments and operational costs', to clarify that the applicability of some specific BAT (e.g. ESP, wet gas scrubber, COS converter) may be restricted for existing units. |
| 5 | CZ, EL, ES and CONCAWE | A dissenting view was expressed by CONCAWE, the Czech Republic, Greece and Spain who consider that the BAT-associated emission level (BAT-AEL) ranges for emissions to air of SO ₂ from the catalytic cracking units should be the following: <ul style="list-style-type: none"> • 100 – 1 000 mg/Nm³ for existing units in full combustion mode, • 100 – 1 700 mg/Nm³ for existing units in partial combustion mode. |
| 6 | CZ, EL, FI, PT, and CONCAWE | A dissenting view was expressed by CONCAWE, the Czech Republic, Greece, Finland and Portugal who consider that the BAT-associated emission level (BAT-AEL) ranges for emissions to air of NO _x from the catalytic cracking units in full combustion mode should be complemented by the following footnote (²): (²) In some FCC designs, all secondary techniques include applicability restrictions and in case the NO _x additive reduction efficiency is limited to less than 50 %, NO _x levels up to 400 mg/Nm ³ may occur. |
| 7 | NL and EEB BE and SE | A dissenting view was expressed by the Netherlands and the EEB who consider that the BAT-associated environmental performance level (BAT-AEPL) range for the sulphur recovery efficiency of sulphur recovery units should be 99.5 – 99.9 % for both new and existing units. A dissenting view was expressed by Belgium and Sweden who consider that the BAT-associated environmental performance level (BAT-AEPL) range for the sulphur recovery efficiency of sulphur recovery units should be ≥ 99 % for existing units. |
| 8 | CZ, EL, IT and CONCAWE | A dissenting view was expressed by CONCAWE, the Czech Republic, Greece and Italy who consider that the BAT-AEL range for gas-fired existing combustion units of less than 50 MW should be the following: <ul style="list-style-type: none"> • NO_x: 30 – 300 mg/Nm³. |

In addition, during the final TWG meeting, it was acknowledged that: *'The links between the 'bubble approach' and the implementation of the IED need further legal consideration. The Commission Services will consider the most appropriate way to take into account the outcome of the TWG meeting and to continue the work on this issue over the next months'*.

Consultation of the Forum and subsequent formal adoption procedure of the BAT Conclusions

As a response to the view expressed by CONCAWE, the Czech Republic, Greece, Spain, Finland, France, Italy, Poland, Portugal, Sweden and Slovakia who consider that the BAT conclusions should make reference to the 'bubble' approach, a discussion paper concerning this item including the proposed formulation of a BAT conclusion was presented at the IED forum meeting of 20 September 2013. After discussion, there was a forum consensus on two main principles:

- that a 'bubble' approach should achieve at least the same, or a better, environmental outcome than would be the case under a unit-level application of the BAT-AELs and
- that a 'bubble' approach results in an 'over-performance' against the upper end of the individual BAT-AELs.

In accordance with Article 13(3) of the IED, the forum gave its opinion on the draft Best Available Techniques (BAT) reference document for the Refining of Mineral Oil and Gas as presented at the meeting of the forum of 20 September 2013:

- The forum welcomes the draft Best Available Techniques (BAT) reference document for the Refining of Mineral Oil and Gas as presented by the Commission
- The forum acknowledges the discussions held at its meeting of 20 September 2013 and agrees that the changes to the draft Best Available Techniques (BAT) reference document for the Refining of Mineral Oil and Gas, as proposed in Annex A to the opinion, should be included in the final document. The main changes agreed include:
 - Recommend to use monitoring standards at the beginning of Chapter 3;
 - Correct typos and factual errors (e.g. structure of Section 4.15, missing conversion to SI units);
 - Clarify the BAT on monitoring for emissions to air in combustion units (threshold, SO_x monitoring, exception for metal in gas combustion);
 - Clarify the BAT for coking (venting);
 - Reintroduce in BAT 35 the unintentionally removed two footnotes;
 - Clarify the definition of H/C ratio referred to in BAT 36 footnote 1;
 - Clarify the definition of flue-gas desulphurisation
- The forum reaffirms the comments in Annex B to the opinion as representing the views of certain members of the forum but, on which, no consensus exists within the forum to include them in the final document.

Subsequently, the Commission took the opinion of the IED Article 13 Forum into account when preparing the draft Commission Implementing Decision establishing best available techniques (BAT) conclusions for the refining of mineral oil and gas, which included BAT 57 and BAT 58 on the integrated emission management techniques (i.e. the 'bubble' approach). The IED Article 75 Committee, at its meeting of 24 June 2014, gave a positive opinion on this draft Commission Implementing Decision.

In addition, the Commission also prepared a Commission Implementing Decision establishing the type, format and frequency of information to be made available by the Member States on integrated emission management techniques applied in mineral oil and gas refineries. The IED Article 75 Committee, at its meeting of 24 June 2014, also gave a positive opinion on this draft Commission Implementing Decision.

Subsequently:

- the Commission Implementing Decision 2014/738/EU establishing best available techniques (BAT) conclusions for the refining of mineral oil and gas was adopted on 9 October 2014 and published in the Official Journal of the European Union (OJ L 307, 28.10.2014, p. 38)

- the Commission Implementing Decision 2014/768/EU establishing the type, format and frequency of information to be made available by the Member States on integrated emission management techniques applied in mineral oil and gas refineries was adopted on 9 October 2014 and published in the Official Journal of the European Union (OJ L 315, 01.11.2014, p. 15).

Recommendations for future work

The information exchange revealed a number of issues where further information should be collected during the next review of the REF BREF. These recommendations include:

- Emissions to water:
 - to collect short-term emissions data, expressed both in loads and in concentrations linked to the use of the techniques;
 - to collect and use the data from monitoring of the phenol index instead of phenol.
- Emissions to air:
 - emissions to air of dioxins and furans (PCDD/F) from catalytic reformer units should be further assessed;
 - emissions of metals from FCC units and combustion units should be further assessed (including from gas-firing combustion units);
 - the impact of the use of low N feedstock on NO_x emissions from FCC units should be further studied;
 - specific data should be collected in order to assess the potential detrimental effect of the use of additives for sulphur reduction on dust emissions and the related abatement systems;
 - to reconsider the issue of new combustion units (both gas and multi-fuel firing) as, due to lack of data, no BAT conclusions and BAT-AELs for SO₂ and NO_x have been set for new units;
 - to consider collecting robust data on NO_x emissions from coking processes;
 - to consider the ongoing work in the EU regarding an EN standardisation for diffuse VOC emissions monitoring methods.

Suggested topics for future R&D work

The Commission is launching and supporting, through its Research and Technological Development programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially, these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the European IPPC Bureau of any research results which are relevant to the scope of this document.

8 ANNEXES

8.1 Refinery configurations

Worldwide there are in total approximately 650 refineries. Every year on average between four and six brand new refineries come on-stream, mainly outside Europe (China, India). On the other hand the origin of some of the oldest refineries still in operation dates back to the end of last century. Many of these refineries have been extended and modernised since. Basically there are about 25 typical refinery processes (excluding treatment) used in the refinery industry. The simplest type, the so-called hydroskimming refinery, comprises a minimum of five processing units. Some large and complex refineries can comprise up to fifteen different processing units or more.

In this section four of the most common refinery schemes or configurations will be discussed in detail. The classification of refineries into these configurations is slightly arbitrary. Other approaches do exist, but the main purpose is to illustrate the great diversity of refinery types in existence.

| Configuration | Units included |
|---------------|---|
| 1 | Hydroskimming (Base Scheme) + Isomerisation Unit |
| 2 | Base Scheme + High Vacuum Unit + Fluid Cracking Unit + MTBE Unit + Alkylation Unit + Visbreaker |
| 3 | Base Scheme + High Vacuum Unit + Hydrocracker Unit + Isomerisation Unit (+ Delayed Coker Unit) |
| 4 | Large complex refinery comprising Scheme 2 + Hydrocracker (+ Hydrogen Residue Cracking unit + IGCC + Petrochemical feedstock production + Flexicoker) |

The overall block flow diagrams of the above four configurations are shown in Figure 8.1 to Figure 8.4.

The first diagram is the aforementioned ‘Hydroskimming’ refinery including an Isomerisation Unit. Such a refinery merely produces fuels such as gasoline, kerosene (jet fuel), middle distillates (diesel and light heating oil) and fuel oil, in a ratio determined by the crude oil composition. By adding a Vacuum Distillation Unit and conversion units the atmospheric residue from the Crude Distillation Unit can be converted to lower boiling fuels with higher product values. Two schemes will be discussed, to cover the most commonly used conversion processes, i.e. Fluid Catalytic Cracking and Hydrocracking. The Fluid Catalytic cracker (FCC) configuration (N°2) may include an MTBE unit and an Alkylation unit to increase the production and to improve the quality of the gasoline. A Thermal Cracker or Visbreaker unit is often also included in this scheme to reduce the quantity of the heavy fuel oil. The Hydrocracker configuration (N°3) may include a Delayed Coker unit to reduce heavy fuel production and to maximise light fuels production. The last configuration included in this overview is a large, very complex refinery. Besides a Hydrocracker and a FCC unit, this refinery scheme includes units for the conversion of the vacuum residue, a Residue Hydroconversion unit and an Integrated Gasification Combined Cycle Unit.

The complexity of the above four configurations (Simple, Complex catalytic cracking, Complex hydrocracking, and Very Complex) can be quantified and various approaches prevail in the Industry. One approach is to express each processing unit in its so-called ‘equivalent distillation capacity’ (EDC), and calculate the sum of these EDCs as a total refinery EDC (the crude distillation unit has an EDC of 1 by definition). The complexity is then the sum of EDCs.

Another approach is to express the conversion (of residual material into distillates) of each conversion unit into its ‘catalytic cracking equivalency’, and then to define the refinery complexity as the sum of all the catalytic cracking equivalencies. In comparing refineries, both

the configuration (which units are included) and the complexity (what is the capacity of these units) are important to consider.

Energy requirements will generally increase from configuration 1 to 4 and with complexity. Similar generalisations can be made regarding process water requirements, sulphur production (at same sulphur intake), etc. but qualifications often need to be made. In the schemes that represent the configurations in the following pages, processing units are abbreviated; for more details on these process units, see the Glossary.

8.1.1 Configuration 1: hydroskimming + isomerisation unit

This is the simplest type of refinery, producing fuels by straightforward operations (see Figure 8.1). This type of refinery has a very rigid product distribution pattern; the produced fuels are almost entirely fixed by the type of crude being processed. The production cannot be greatly influenced by changing the operating modes of the various processing units.

Many of the Hydroskimming refineries were built in the fifties and sixties when the demand for all fuels increased significantly, the cost of crude was relatively low and the demand for heavy fuel oil was relatively high. In the seventies and eighties the majority of the Hydroskimming refineries were expanded to include a cracking complex, but quite a lot of Hydroskimming refineries dating from that period are still in operation. In the Crude Oil Distillation Unit the crude oil is fractionated into straight-run naphtha overhead product, kerosene, gas oil side-stream products and atmospheric residue product from the bottom of the column. The straight-run unstabilised naphtha is passed to the Naphtha Hydrotreating Unit to make it suitable for Catalytic Reforming. The hydrotreated naphtha stream is split into a light and a heavy naphtha fraction.

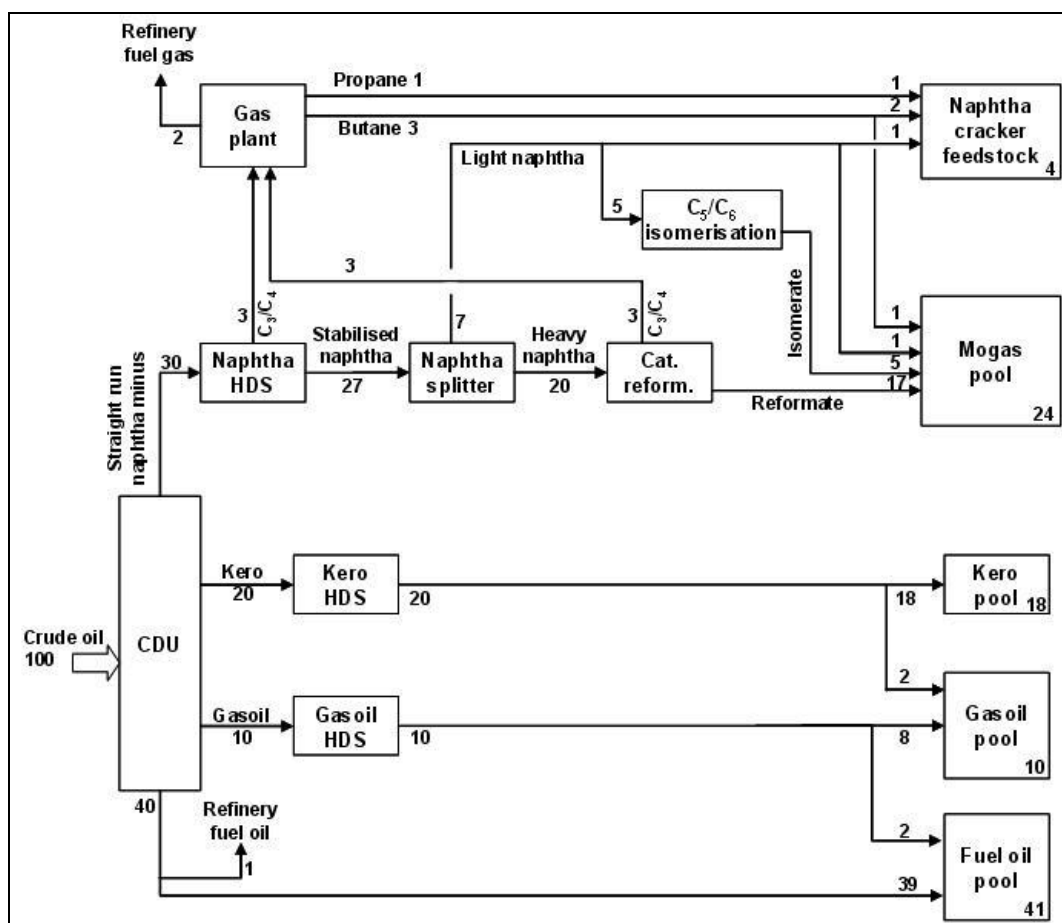


Figure 8.1: Scheme 1: Hydroskimming and isomerisation unit

In the past, part of the light naphtha fraction was used as mogas (motor gasoline) blend component, and the balance was sold as feedstock to Naphtha Crackers. More recently, as a result of the lead (TEL) phase-out programme, many Isomerisation Units are included in the Hydroskimming refineries to isomerise the light naphtha stream. The isomerate produced has a roughly 20 – 25 higher octane number than its feed and compensates for the loss of octane resulting from the lead phase-out. This avoids the complete light naphtha stream being sold as low-value feedstock to Naphtha Crackers. The heavy naphtha fraction from the Naphtha Hydrotreater is upgraded in the Catalytic Reformer to a high-octane gasoline-blending component. The hydrogen from the Catalytic Reformer is used to desulphurise the gas oil and naphtha. Normally two grades of gasoline are produced in a refinery, regular and premium gasoline. These grades of gasoline are produced by blending different ratios of isomerate, reformat and butane. Saturated light hydrocarbons from the CDU Naphtha Hydrotreater, Isomerisation Unit and Catalytic Reformer Unit are sent to the Gas Plant. Propane from the Gas Plant is either sold directly as propane product or blended with butane to be sold as LPG. A proportion of the butanes produced in the Gas Plant is used as blend stock for the mogas pool, the remainder of the butanes are either blended with propane to be sold as LPG or directly sold as butane product. The components lighter than propane are sent to the refinery fuel gas system. Straight-run kerosene is often hydrotreated in the Kero Hydrotreating Unit (or kero HDS) and run down as jet fuel. Normally a portion of the hydrotreated kerosene is used as a blending component for the automotive diesel oil pool.

Straight-run gas oil is hydrotreated in the Gas Oil Hydrotreating Unit to reduce its sulphur content. Automotive diesel oil is produced by blending desulphurised kerosene with desulphurised gas oil. Heating oil and marine diesel oil (MDO) are produced by blending desulphurised gas oil with straight-run gas oil. Both products have higher maximum allowable sulphur contents than diesel oil. Heavy fuel oil is produced from atmospheric residue with adjustment for viscosity and sulphur content by addition of desulphurised gas oil. In some cases the atmospheric residue is thermally cracked. This is not indicated in the configuration scheme. The sour off-gases from the Naphtha Hydrotreater, the Kerosene and Gas Oil Hydrotreating units (or Gas oil HDS) are treated in the Amine Treating Unit to remove H₂S and other sour components present, prior to being sent to the refinery fuel gas system. The sour LPG stream from the Naphtha Hydrotreater is also treated in the Amine Unit to reduce its sulphur content before combining with the sweet LPG stream from the Catalytic Reformers. Sour waste water from all process units is stripped, prior to utilisation as wash water in the Desalter and final purification in Effluent Water Treating facilities. The sour off-gas from the Sour Water Stripper is combined with the H₂S-rich off-gas from the Amine Unit and sent to a Sulphur Recovery Unit (SRU), where the H₂S is converted to elemental sulphur, and a nearly sulphur-free off-gas is vented to the atmosphere.

8.1.2 Configuration 2: catalytic cracker configuration

Scheme 2 is a configuration whereby the Hydroskimming refinery is extended with a High Vacuum Unit (HVU), a Fluid Catalytic Cracking Unit (FCC unit) and a Visbreaker Unit (VBU). In this refinery configuration, a considerable part of the atmospheric residue is converted into lighter fuel components (see Figure 8.2.). As a result, the production of residual fuel oil and/or the export of atmospheric residue is considerably reduced. FCC units are specifically designed to increase the production of gasoline. Depending on the refinery market and strategy, a significant quantity of kerosene can also be produced, when the heavier fraction of the catcracked naphtha is separated and hydrotreated along with the straight-run kerosene product. The overall yield of middle distillates is also increased due to the production of 'light cycle oil'.

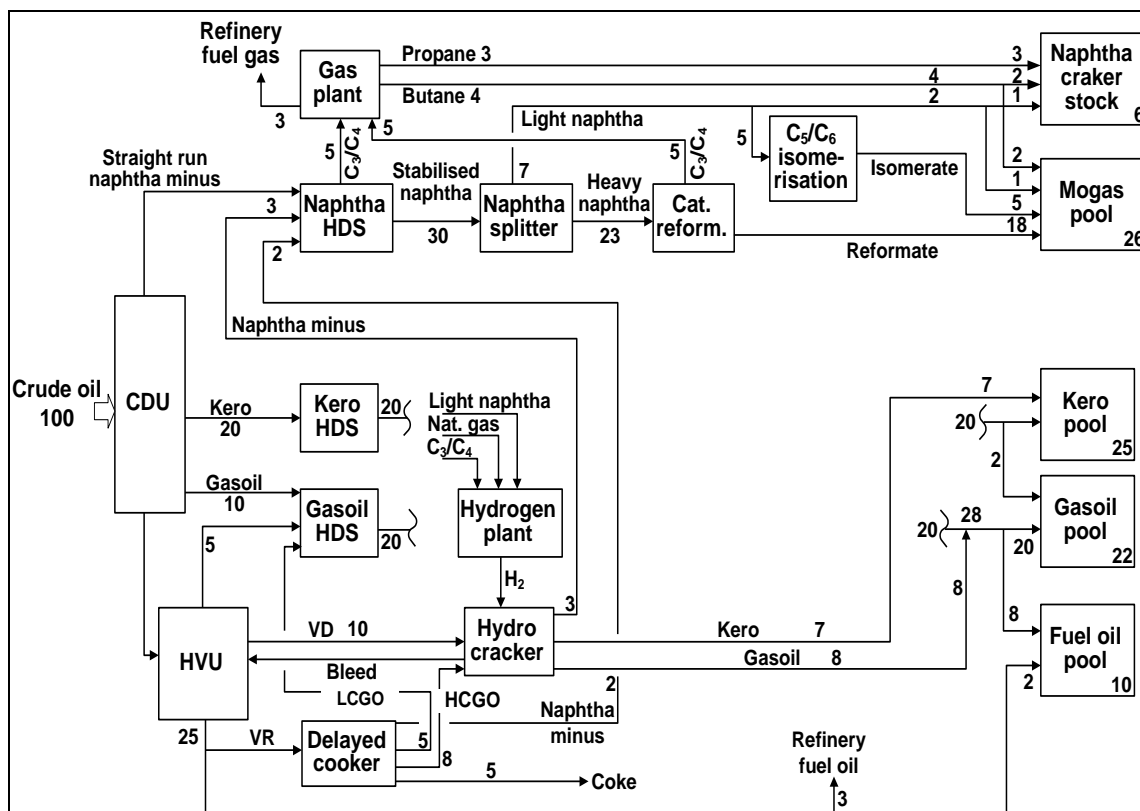


Figure 8.3: Scheme 3: Hydrocracker configuration

This type of refinery has a higher degree of flexibility with respect to either maximum gasoline or maximum middle distillate production, whereas a FCC configuration is primarily focused on increased gasoline production. About 15 % of the existing refinery complexes in Europe have already been extended with a Hydrocracker. It should be noted that such extensions require a relatively high capital investment and high energy consumption compared to the installation of a Catalytic cracker.

8.1.4 Configuration 4: complex refinery with hydroconversion and IGCC

Scheme 4 is a refinery with a Hydrocracker and additional ‘deep conversion’ with a Residue Hydrocracker and/or a Gasification Unit (IGCC), so that even more conversion capacity for heavier feedstocks is introduced (see Figure 8.4). This is an example of a large complex refinery, and it includes some options to produce high-value petrochemical feedstocks. This extended range of heavy residue conversion techniques can in principle eliminate the need for mixing heavy residue to the fuel oil pool or can process more heavy crude oils. The Residue Hydrocracker, i.e. Hycon, H-oil Unit or other types of Residue Hydrocrackers, converts vacuum residues to high-value transportation fuels, e.g. gasolines, kerosene and diesel. The addition of a Residue Hydrocracker to a refinery provides considerable flexibility and increases production of gasoline and middle distillate fuels at the expense of fuel oil. The IGCC converts the visbreaker residue to power, steam, hydrogen, and some waste streams. The main advantage of this arrangement is the production of hydrogen by use of low-value vacuum residue instead of the more valuable light naphtha, other light hydrocarbon streams or natural gas. Moreover, the fuel oil production is reduced and the production of LPG and diesel fuels is increased.

8.2 Refinery feedstock, intermediates and products

This section contains a brief explanation of the chemical and physical properties of feedstock, intermediates and products available within a refinery. Because some of the terms may vary from country to country, this annex gives a short description of how these names are used within this document. Moreover, this annex gives a short overview for non-expert readers.

8.2.1 Crude oil

Crude oil is a mixture of hydrocarbon compounds (95 – 99 % w/w) of different chemical composition and molecular structures with some impurities. Most of these impurities, such as sulphur, nitrogen, vanadium and nickel are chemically bound to the hydrocarbon structures. Others, such as sand/clay, water and water-soluble salts of zinc, chromium and sodium are present as inorganic material.

The hydrocarbons in crude oil are a mixture of three chemical groups: paraffins (straight and branched chains are called normal- and iso-paraffins), naphthenes (saturated rings or cycloparaffins) and aromatics (one or more unsaturated rings). The most used rough distinction between crude oil types is sweet or sour. Sweet crude is normally low in sulphur and lightly paraffinic. Sour crude is usually high in sulphur and heavily naphthenic.

The composition of the crude is the most important parameter in establishing the range and quality of products that may be produced from a refinery. The impurities of the crude, which usually make up 1 – 5 % of the total, are also very important in establishing the value of the crude and the difficulties in converting it into marketable products. The most important impurity of crude oil is sulphur, which is present largely in the form of organic compounds such as mercaptans and sulphides. Some elemental sulphur, H₂S, and FeS may also be present but only in small quantities. The total sulphur content may be as low as 0.04 % w/w or as high as 5 % w/w. Crudes containing more than 0.5 % w/w S are commonly referred to as 'sour' and the others as being 'sweet'. In general, the sulphur content increases in the higher boiling fractions.

Examples of crude types processed in European refineries are shown in Table 8.1. A distinct shift in crude oils processed in European refineries took place between 1993 and 1997, from Middle East crude oils to 'North Sea' crudes. Market forces mainly caused this and this trend could therefore easily reverse. CONCAWE has reported that the average sulphur content processed in European refineries decreased from 1.45 % in 1979 to approximately 1.0 – 1.1 % from 1985 onwards. The availability and marketing of low-sulphur crude oils has helped the European refineries to reduce SO₂ emissions and to some extent also the emissions of NO_x.

Table 8.1: Examples of crude oil types and compositions

| Crude origin | Crude Oil | Density kg/m ³ | Kinetic viscosity mm ² /s | Sulphur % w/w | Vanadium mg/kg | Nickel mg/kg |
|--------------|---------------|---------------------------|--------------------------------------|---------------|----------------|--------------|
| Middle East | Arabian Light | 864 | 5.18 | 1.91 | 23.7 | 4.6 |
| | Iranian Heavy | 870 | 7.85 | 1.67 | 68.2 | 21.4 |
| | Arabian Heavy | 889 | 14.54 | 2.92 | 69.8 | 22.3 |
| | Iranian Light | 860 | 5.11 | 1.46 | 55.2 | 17.0 |
| | Kuwait | 870 | 6.90 | 2.47 | 32.9 | 9.6 |
| North Sea | Statfjord | 830 | 2.70 | 0.26 | 1.5 | 0.7 |
| | Oseberg | 845 | 3.47 | 0.24 | 1.6 | 0.8 |
| Russian | Ural | 864 | 5.41 | 1.55 | 37.1 | 12.2 |

The next two tables show the metal content of crude oil. Nickel and vanadium are present as porphyrin systems in the crude oil. In order to determine heavy metals in crude, sampling is of crucial importance. More information about that can be found in [150, Dekkers, Daane 1999]

Table 8.2: Metal content of different crude oils

| Source | Metals (ppm) | | | |
|---------------|--------------|------|-------|-----|
| | Fe | Ni | V | Cu |
| East Texas | 3.2 | 1.7 | 12 | 0.4 |
| West Texas | 5.1 | 4.8 | 7.9 | 0.4 |
| Mirando | 7.6 | 1.9 | 1.4 | 0.5 |
| Jackson | 4.4 | 1.8 | 0.9 | 0.1 |
| Scurry County | 3.4 | 1.0 | 0.8 | 0.2 |
| Wilmington | 28 | 46.0 | 41.0 | 0.6 |
| Santa Maria | 17 | 97.0 | 223.0 | 0.3 |
| Kettleman | 24 | 35.0 | 34.0 | 0.4 |
| Ventura | 31 | 33.0 | 49.0 | 1.1 |
| Tibu-Petrolea | 1.6 | 9.0 | 60.0 | 0.9 |
| Kuwait | 0.7 | 6.0 | 77.5 | 0.1 |
| Mid-Continent | 3.8 | 4.2 | 7.9 | 0.3 |
| Kansas | 5.8 | 5.8 | 20.8 | 0.4 |
| Morocco | | 0.8 | 0.6 | 0.1 |
| Redwater | 3.4 | 10.6 | 4.5 | 0.1 |

Source: Speight, J 0 - The Chemistry and Technology of Petroleum, Marcel Dekker Inc.1980

Table 8.3: Range of metals and other elements contents found in crude oils

| Element | Concentration (ppm) | | |
|---------|---------------------|---|------|
| V | 5.0 | – | 1500 |
| Ni | 3.0 | – | 120 |
| Fe | 0.04 | – | 120 |
| Cu | 0.2 | – | 12.0 |
| Co | 0.001 | – | 12 |
| Si | 0.1 | – | 5.0 |
| Ca | 1.0 | – | 2.5 |
| Mg | 1.0 | – | 2.5 |
| Zn | 0.5 | – | 1.0 |
| Al | 0.5 | – | 1.0 |
| Ce | 0.001 | – | 0.6 |
| Zr | 0.001 | – | 0.4 |
| Ti | 0.001 | – | 0.4 |
| Sn | 0.1 | – | 0.3 |
| Pb | 0.001 | – | 0.2 |
| Hg | 0.03 | – | 0.1 |
| B | 0.001 | – | 0.1 |
| Ga | 0.001 | – | 0.1 |
| Ba | 0.001 | – | 0.1 |
| Sr | 0.001 | – | 0.1 |

A report [150, Dekkers, Daane 1999] has shown that the quantities of Cadmium, Zinc, Chromium, Copper and Arsenic in the crudes are indeed much lower than traditionally assumed. Reasons for this include improper analytical techniques and contamination during sampling. Table 8.4 shows the results achieved in the above-mentioned report.

Table 8.4: Content of certain metals in some crude compared to other published data

| Metal | Concentration ($\mu\text{g}/\text{kg}$) | |
|--|---|-------------------------------|
| | | Published data ^(*) |
| Arsenic | 4 – 37 | 0.2 – 26 200 |
| Cadmium | 0.40 – 4.9 | 0.10 – 29.1 |
| Chromium | 12 – 240 | 1.5 – 3 170 |
| Copper | 10 – 195 | 30 – 7 180 |
| Zinc | 59 – 1 090 | 25 – 19 500 |
| (*) Published data from several sources reflected in the report. Source: [150, Dekkers, Daane 1999] | | |

Physical properties and characteristics of crude oil

Crude oil is a mixture of many compounds and, apart from the lightest components, the characterisation by a complete chemical analysis is almost impossible. As a result, the general physical properties are expressed in terms of simple parameters, which can be quickly estimated. The underlying nature of the crude is then derived from this information by comparison with corresponding parameters from known feedstocks. Most of these parameters are not limited to crudes, but may be used for most petroleum products as well. One of the simplest crude properties to measure is the specific gravity, normally expressed in terms of the °API. Crudes are often classified as being ‘heavy’ or ‘light’ according to their °API, the heavy being less than about 28 – 32 °API and the light over 32 – 35 °API.

8.2.2 Refinery intermediates and products

There are over a hundred refinery products, including gaseous and liquid refinery fuels for domestic and industrial use, fuel for most forms of transport, lubricating oils for all types of machinery and the basic raw materials for the petrochemical industry. Individual refineries do not usually supply the full range of possible products, but try to select those most suited to the quality of the crude feed, the available processing equipment and the local market requirements. The composition of a product will vary between refineries, being a function of crude type and refining processes used, but the overall quality will meet the product specifications prevailing for a given market. The major refinery product groups are shown in Table 2.1 by refinery process unit. A short description of the product groups follows.

Refinery fuel gas (RFG)

Refineries use the C_1/C_2 fraction as refinery gas to cover part or most of their fuel requirements. Refinery gas can also contain H_2 . An amine wash is normally used to extract H_2S .

Liquefied petroleum gas (LPG)

Sometimes C_3 and C_4 components are also used for refinery fuel, but most of the C_3 and C_4 components will be sold as liquefied petroleum gas (LPG), which is used as a fuel for numerous applications. LPG is sold either as a mixed LPG fraction or as separated C_3 and C_4 fractions. The liquid propane normally contains a minimum of 95 % w/w C_3 compounds, the remainder being C_2 and C_4 . Butanes and butenes are also used as a petrochemical feedstock for the manufacture of MTBE, acetic acid, solvents, polybutylenes, and rubber.

Naphtha and chemical naphtha

Naphtha is the raw gasoline range fraction from crude oil distillation. As well as gasoline production, in some cases, naphtha is used as the feedstock for petrochemicals production.

Gasoline

Gasoline, the fuel for motor cars and light aircraft, represents the highest volume and one of the more valuable refinery products. Automotive gasoline, which is by far the most important gasoline type, consists of a complex mixture of hydrocarbons ranging from C_4 to C_{10} , boiling between 38 °C and 205 °C. Most refiners produce gasoline in three or four octane grades, the

principal difference being the anti-knock performance. Mogas is a term normally used for motor gasoline.

Jet fuel (kerosene, avtur)

Jet fuel is the name given to kerosene or kerosene blends used as fuel in aviation turbines (hence also called Avtur) by both commercial aviation and military aircraft. For most refineries the primary source of jet fuel blending stocks is the straight-run kerosene fraction (C₈ - C₁₂) from the atmospheric crude unit. For a refinery with a Hydrocracker, kerosene boiling range hydrocarbons from this unit can also meet jet fuel specifications, and is a major contributor to jet fuel production. Hydrotreated light Coker gas oil and thermally cracked gas oil can also be used as blending stock. In some developing countries, kerosene is still the primary fuel for cooking and domestic heating.

Diesel oil/heating oil/gas oil

Diesel fuels are produced by blending of kero and gas oil fractions from the crude distillation unit and gas oil fractions of the high vacuum unit and from conversion units. An upgraded and flexible processing scheme for desulphurisation of blending components is necessary in most refineries in order to arrive at the currently required and future sulphur specifications (500 ppm currently, 350 ppm from 2000 and 50 ppm from 2005 onwards). Light heating oils (kero/diesel fraction) are typically used for small domestic applications.

Middle distillates/distillate fuels

Alternative names for the fuels in the kerosene and gas oil boiling ranges.

Fuel oils

Fuel oils cover a very wide range of applications and are produced in a variety of grades. Gas oils are sometimes referred to as fuel oils, but in Europe the term is usually used to describe heavy fuel oils (atmospheric residue) which are used for electricity etc. Heavy fuel oils are used for electricity or power generation by utility companies, or sold as bunker fuel oil for seagoing vessels. Refineries use heavier fractions from crude oil distillation, from vacuum distillation or from visbreaking for generation of heat, electricity and steam in their furnaces and boilers.

Heavy fuel oils consist largely of the residue remaining from the distillation of crudes. These residues consist of large hydrocarbon structures containing components that require additional processing to convert them into more valuable, lighter products for use in gasoline and diesel engines. These residues generally have a high sulphur and ash content, are mostly very viscous and will therefore be blended with lighter gas oils in order to sell them as a commercial fuel for ships and utilities.

Lubricating oils, wax and greases

Lubricating oil feedstocks are produced from the atmospheric residue by fractionation under vacuum. The oil cuts produced from the vacuum distillation column are further processed to remove unwanted impurities (solvent extraction and dewaxing) and blended with miscellaneous additives (both organic and inorganic in nature) to give lubricating oils of various grades. Lubricating oils can be modified by mixing with thickening agents such as soap, clay or silica gel to produce lubricating greases. Dewaxing yields paraffinic or microcrystalline wax that is usually subjected to hydrofinishing to remove colours, odours and potentially carcinogenic hydrocarbons for domestic applications.

Bitumen

Bitumen (referred to as asphalt in the US) is used mainly for paving roads but also for a number of other applications, such as materials for roofing. The basic source of bitumen is the residue remaining after vacuum distillation of crude. The residue can also be treated by blowing with air at high temperature (bitumen blowing process) to increase the asphaltene content.

Petroleum coke

Petroleum coke is the residue remaining after destructive distillation of petroleum residue in a delayed coking unit. It is widely used as fuel in the cement and steel industry. It can also be used as a fuel for power plants if the sulphur content is low enough. Coke also has non-fuel applications as a raw material for many carbon and graphite products.

Table 8.5: Example of petroleum coke analysis

| Petroleum coke analysis used in oxygen-blown gasification | |
|--|--------------|
| Ultimate analysis | % w/w |
| Carbon | 87.1 – 90.3 |
| Hydrogen | 3.8 – 4.0 |
| Oxygen | 1.5 – 2.0 |
| Nitrogen | 1.6 – 2.5 |
| Sulphur | 2.1 – 2.3 |
| Proximate analysis | % w/w |
| Volatiles | 9.0 – 9.7 |
| Fixed C | 80.4 – 89.2 |
| Moisture | 0.9 – 10.2 |
| Ash | 0.2 – 0.4 |
| <i>Source: [175, Meyers 1997]</i> | |

Sulphur

Sulphur is basically a by-product of refining resulting from the removal of sulphur compounds from the main hydrocarbon product streams. The quantity of sulphur produced by a refinery depends on the amount present in the crude and the desulphurisation and sulphur recovery capacity installed. It is a valuable product which is mainly used as the raw material for sulphuric acid manufacture.

Relationship between feed (typically crude oil) and products

As a broad generalisation, it is true to say that any crude can be processed into any reasonable selection of products by a suitable choice of refining unit operations. The cost of production will depend on the refining units required, which in turn depend on the crude selected. In theory the production cost can be minimised by careful selection of the crude. In practice, however, refinery designs are often compromised by factors such as: the changing availability, price and composition of crudes and changing market demands for product slate and specifications. A few relatively simple crude properties can indicate the feasibility of processing a particular crude (mix) with a given refinery complex.

In general, it is found that the heavier the crude, the higher the quantities of sulphur, Conradson carbon and heavy metals, and the lower its hydrogen content. Heavy crudes are also more difficult to process. Heavy crude normally results in high fuel oil production while light crude is more appropriate for a high gasoline and middle distillate production. Other simple property indicators are sulphur content and pour point.

In order to evaluate the properties of the various likely products such as gasoline octane rating, the aromatics content of kerosene, etc., it is necessary to distil the crude and analyse the fractions boiling within different boiling ranges. This will give information on the process units that may be required for quality improvement, such as desulphurisation facilities, a reformer unit or an aromatics extraction plant. The residue fractions can be similarly analysed to give more detailed information on the conversion units that may be appropriate.

8.3 Cost-effectiveness of implementation of some techniques

8.3.1 Basic concepts for cost-effectiveness analysis

The ECM BREF [67, COM 2006] provides assistance to both Technical Working Groups (TWGs) and permit writers when considering the environmental and economic conflicts that can occur when determining which techniques to implement under the IED.

According to this document, a cost-effectiveness analysis is described as follows:

The basic concept is simple: one can spend a euro only once. In the context of environmental policy this means that the aim is to achieve highest environmental yield for each euro invested for environmental purposes.

The most explicit way to compare costs and benefits of a measure is to monetarise both and compare them in a cost benefit analysis (CBA). When the comparison shows that the benefits outweigh the costs, this indicates that the measure represents a worthwhile investment. If different alternative measures give positive results, the measure with the highest result is the one offering the highest overall value for money. However, such a cost benefit analysis requires a lot of data and some benefits are difficult to monetarise.

A cost effectiveness analysis is more simplified than a CBA as environmental benefits are quantified but not monetarised. This type of analysis is typically used to determine which measures are preferable to reach a specific environmental target at the lowest cost.

Cost effectiveness (CE) of a technique typically is defined as:

CE = annual cost/annual reduction of emissions (e.g. 5 EUR/kg VOC reduced)

In the context of determination of BAT, the use of the CE concept is not straightforward.

However, ranking BAT options on the basis of ascending CE is useful, e.g. to exclude options that are unreasonably expensive in comparison with the environmental benefit obtained. '

8.3.2 Basic hypothesis and assumptions used in the REF BREF for economics

To enable an easy comparison, the following assumptions have been commonly used to estimate the abatement cost calculations.

- The annualised capital charge (ACC) is 7.4 % (equivalent to a 4 % interest rate applied over a 20-year write-off).
- The scaling rule for cost of a unit sized MW compared to the reference unit MW_{ref} is given by:

$$\text{Cost}_{\text{unit MW}} = (\text{MW}/\text{MW}_{\text{ref}})^{0.6} \text{Cost}_{\text{unit MW}_{\text{ref}}}$$

- The reference fixed operating cost is 4 %/year of the capital cost.

References

[67, COM 2006] [139, CONCAWE 6/11 2011]

8.4 Description of zeolites

Zeolites are widely used in industrial processes or laboratories (Sherman, 1999). They are microcrystalline aluminosilicates of natural or synthetic origin, whose structure is formed by rings consisting of tetrahedral AlO_4^- and SiO_4 are interconnected by oxygen atoms. The negative charges of Tetrahedrons- AlO_4^- cations are compensated by the compensation, present in various locations within the porous structure, which may be replaced by other cations by ion exchange full or partial (Breck, 1974).

The structure of zeolites is an open structure with large pores and channels. After complete dehydration of a zeolite, the channel can be filled with a variety of other molecules. The adsorption process is selective and depends on the particular structure of the zeolite and the size of molecules to be adsorbed. For this reason, zeolites are also called 'molecular sieves'.

Depending on the number of oxygen atoms that form the openings of pores, zeolites can be classified into extra-large pore zeolites ($>9 \text{ \AA}$), large pore zeolites ($6 - 9 \text{ \AA}$), mean pore zeolites ($5 - 6 \text{ \AA}$) and small pore zeolites ($3 - 5 \text{ \AA}$), where access to the interior of the pore takes place, respectively, through rings of 18, 12, 10 or 8 atoms of oxygen (Giannetto, 1990).

The acidity of zeolites is a very important property that depends not only on the material structure, but also other parameters such as total number of Brönsted acid sites and Lewis, and the strength and location of these centres (Serralha, 2001).

The Brönsted acidity is based on the existence of protons as cations compensation. This type of acid depends strongly on the structure and topology of zeolite, the chemical composition and surrounding environment, particularly the molar ratio Si/Al.

There is usually an increase in the strength of Brönsted acid sites with increasing Si/Al ratio. The NaY zeolite has a Si/Al ratio greater than 1.5 (Giannetto 1990), the NaA zeolite a ratio of 1, it is less acidic.

8.5 Soil and groundwater monitoring – An example

Description

See also Section 3.26.

As illustrated in Figure 8.5, the primary objective of a groundwater monitoring network is to:

- provide an access point for measuring groundwater levels;
- collect samples that accurately represent *in situ* conditions at the specific point of sampling.

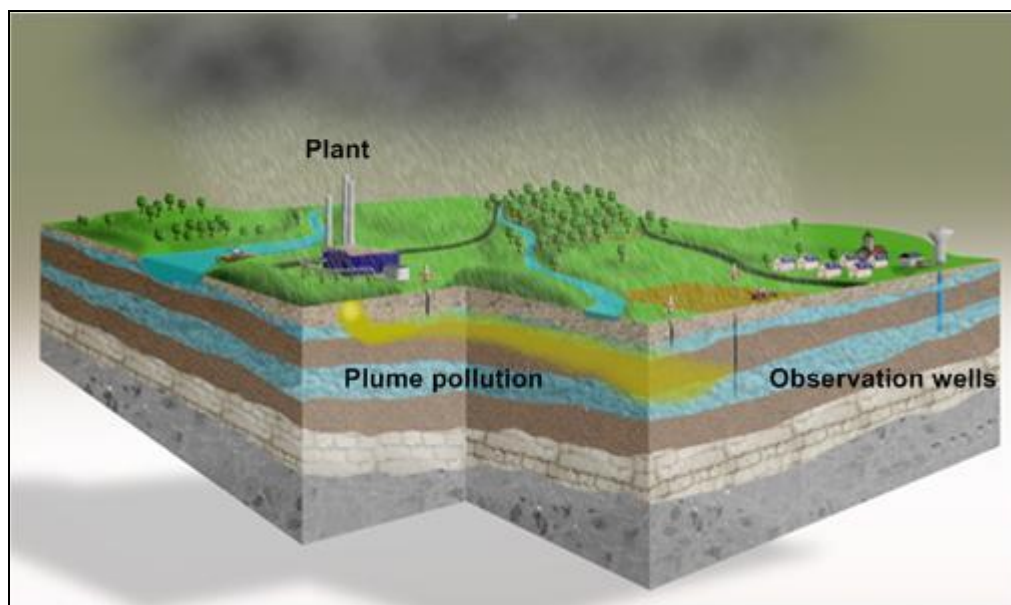


Figure 8.5: Example of a monitoring network in a case of groundwater pollution

Achieved environmental benefits

When properly designed and implemented, a groundwater monitoring system allows to:

- determine the flow direction and groundwater table profile;
- detect the release of pollutants from a suspected or known source;
- determine the extension of the polluted area;
- help design a management strategy and monitor the effectiveness and efficiency of its implementation;
- act as an alert system (in the event of plume advancement);
- extrapolate the concentration of pollutants in the contaminated area and support a risk assessment.

Cross-media effects

Two important points are to be considered when a monitoring network is implemented:

- the risk of cross-contamination of adjacent groundwater, from one borehole to another and/or vertically within a borehole from a contaminated to an uncontaminated zone;
- the cross-contamination of adjacent surface water with contaminated purge groundwaters should be prevented. Adequate measures should be taken, and permits should be obtained for the disposal or release of related effluents.

Operational data

The different steps and operational data required to define, implement and use a groundwater monitoring network can be summarised as explained in Figure 8.6. The installation of an

adequate monitoring network (steps 1 to 3) is an iterative process, and the interpretation of results (step 6) can lead to modifying it.

Step 1:

The concept model is based on a preliminary analysis of data that should be collected on the following aspects, including:

- geological and hydrogeological conditions (fractured, alluvial or karstic);
- existing observation wells (piezometers), taking into account the eventual accumulation of sediments at the bottom of the well;
- potentially contaminating substances (volatile, miscible or immiscible contaminants), classified as light non-aqueous phase liquids (LNAPLs) or dense non-aqueous phase liquids (DNAPLs);
- other anthropogenic influence (existing pollution, pumping well, irrigation, ...);
- public priority protection targets.

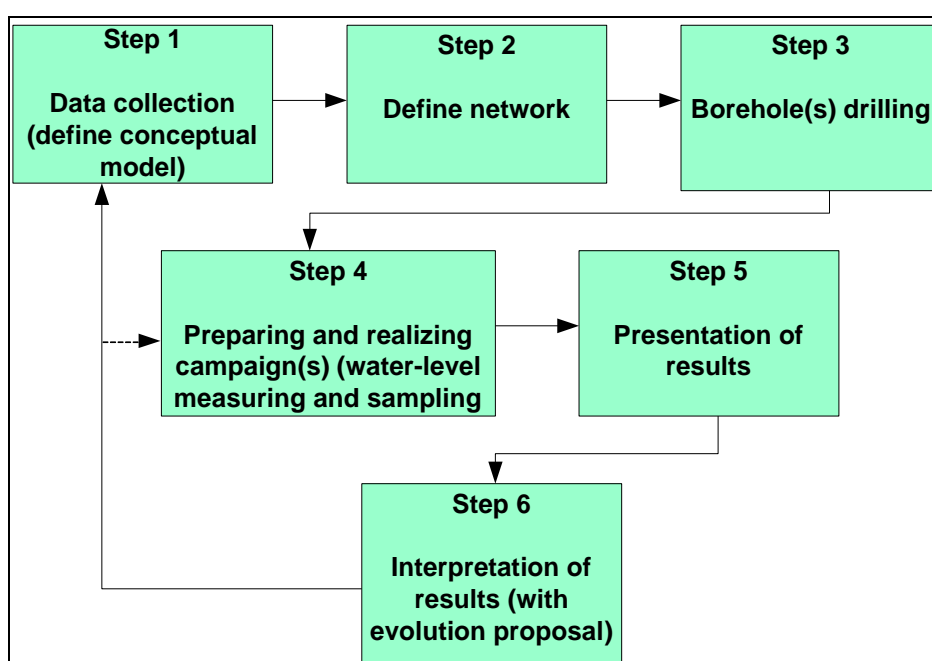


Figure 8.6: Main steps for the implementation of a groundwater monitoring system

Step 2:

This information affects the second step and the monitoring design/strategy, in particular on the well locations, screening levels, drilling and installation methods, selection of parameters, purging and sampling frequency and procedures. Usual frequencies are in the range of 2 – 6 months, site-specific adaptation may be needed. At this stage, particular precautions and related operational choices may be taken, in particular:

- For each pathway monitored, the implementation of a minimum 3 wells is required (1 upstream for comparison of upgradient conditions to background quality, and 2 downstream for allowing groundwater flow direction by triangulation. (See Figure 8.7).
- In the presence of a pure phase, inappropriate purging can lead to redistribution or spreading of the contaminants: low flow purging is thus recommended (micropurging).
- For a DNAPL, sampling may also need to be performed at the bedrock of the aquifer in order to ensure collection of contaminated groundwater from the plume (as illustrated in Figure 8.8).

- A low-flow sampling method should be preferred in case of volatile compounds. Other specific procedures based on local expert requirements can be used to achieve the same results.

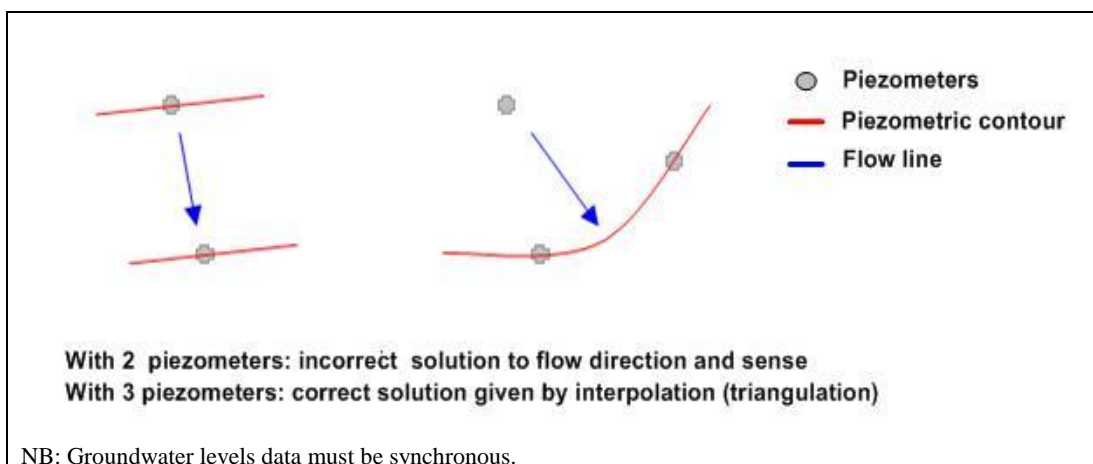


Figure 8.7: Good practice to determine the flow direction

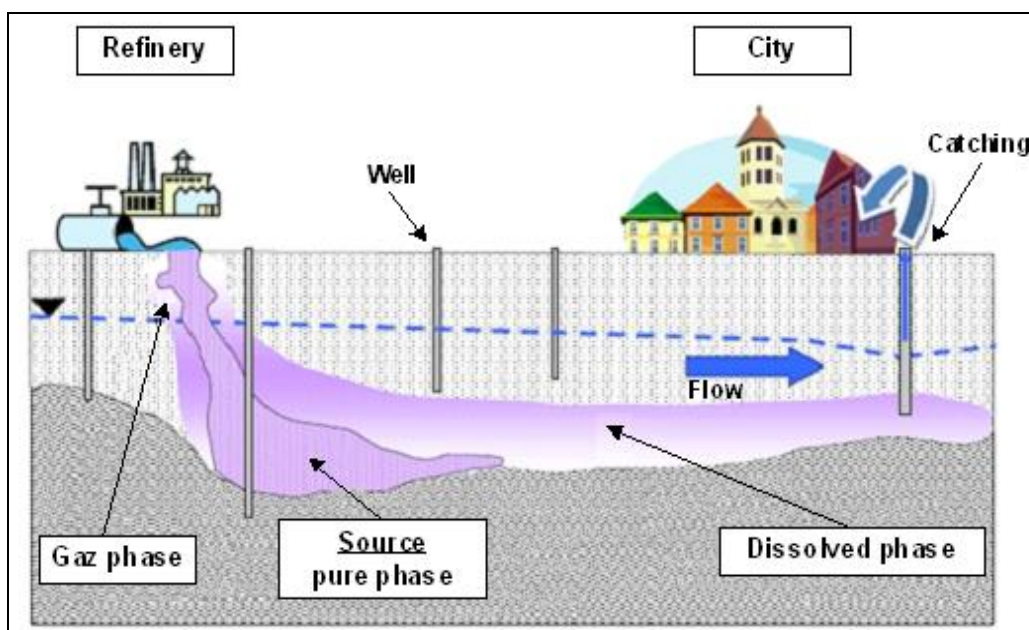


Figure 8.8: Example of DNAPL plume migration in groundwater

Steps 3 to 4: Appropriate standards or guidances might be followed, for example, the ‘Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells’ (US EPA, March 1991) and the ISO 5667 – 11 ‘Guidance on sampling of groundwater’. Laboratories performing the analyses should be accredited for each substance analysed and must achieve the analytical performances set (i.e. limit of quantification). Quality control procedures should also cover the prevention of drilling and sampling equipment contamination.

In the case of oil refineries, the following measures and precautions in particular should be taken:

- the monitoring of the following parameters and substances can be recommended (to be adapted to the context): BTEX, PAH, Total Petroleum Hydrocarbons, pH, temperature and conductivity;

- well construction materials (PVC or HDPE) should be selected in order not to interact with contaminants or modify the composition of the groundwater;
- on sites with aged contamination, multilevel sampling wells can be used for sampling, in order to be able to draw a detailed three-dimensional groundwater contamination profile (e.g. DNAPL).

Steps 5 to 6: the presentation of results will be facilitated using cartographic tools for piezometric and plume mapping, and chronicles of piezometric and concentration data. Figure 8.9 shows an example of a groundwater levels map based on a rather large number of piezometric wells, and developed using a kriging interpolation software; the rectangle corresponds to the refinery footprint. In more simple cases based on a 3 – 4 set of piezometers, an interpolation may be achieved only by triangulation. Seasonal evolution should be taken into account for the interpretation of these results.

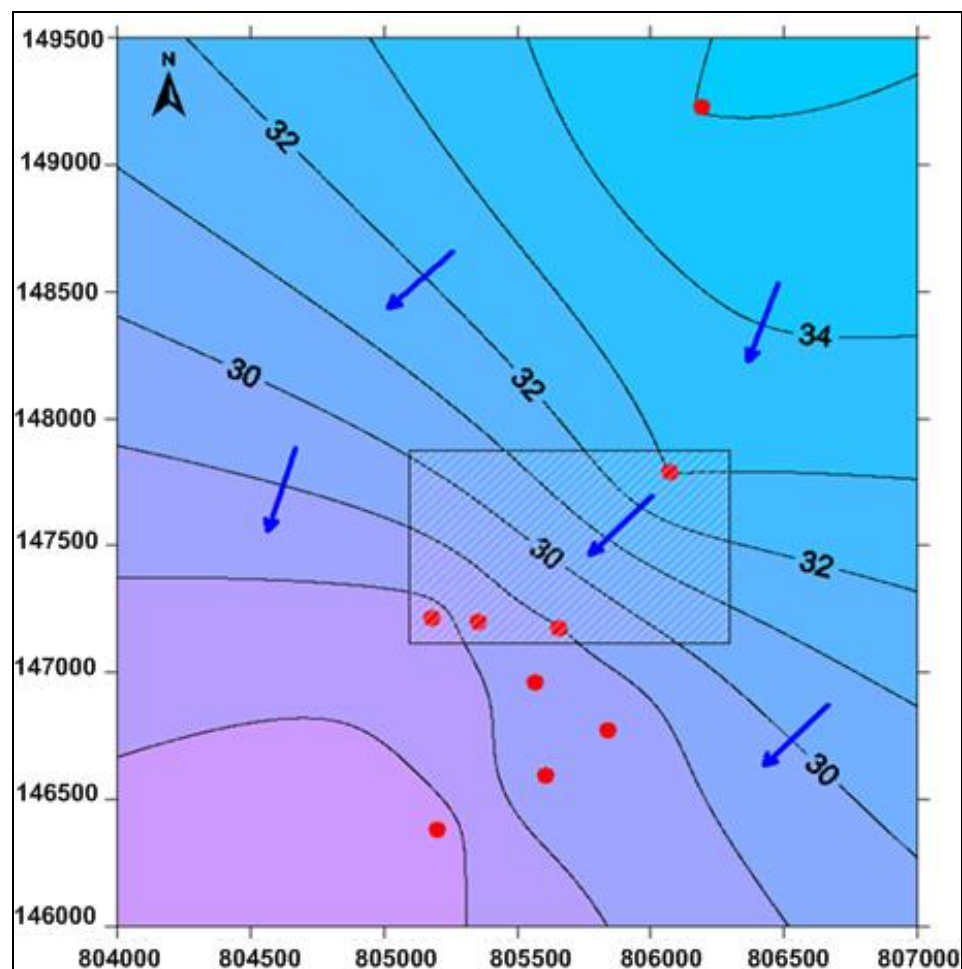


Figure 8.9: Example of groundwater levels map indicating the flow direction and sense (kriging interpolation)

Applicability

Applicable to any new and existing refinery or part of refinery.

Economics

The cost of this technique varies very much, depending in particular on the number of monitored wells, substances, and measuring campaigns.

As an example, the cost for the implementation of three piezometers at a depth of 8 – 10 metres (for alluvial aquifer) is estimated (2010) at around EUR 8 000 – 12 000 for steps 1 to 3. The

cost of a campaign (3 piezometers, sampling, analysis and interpretation), for steps 4 to 6, is estimated at around EUR 1 500 – 2 000 for the monitoring of BTEX, PAH, Total Petroleum Hydrocarbons, pH, temperature and conductivity. The monitoring campaign is usually realised twice a year.

Driving force for implementation

Prevention and early detection of groundwater pollution. Monitoring of old site historic contamination in order to prevent, reduce and manage potential or actual health and environmental impacts.

Example plants

In France, groundwater monitoring is applied in all refineries.

References

[38, INERIS 2009]. TWG FR 2010

8.6 Air emissions – The 'Bubble approach': a methodology

This annex includes 4 appendixes named A to D

Introduction

To prevent the emission of pollutants in the atmosphere, the REF BREF proposes BAT-AELs for specific refining processes or combustion.

One operator could take appropriate measures in order to comply with these values 'stack by stack or unit by unit'.

A specific approach based on a 'bubble concept' can nevertheless be used by the competent authority to regulate one refining site. It will lead to a single value being defined as a target for the refinery as a whole.

This annex aims to provide an example methodology to make the relevant calculations.

This approach takes into account the specificity of the refining sector, in particular the following factors:

- the recognised complexity of refining sites, with a multiplicity of combustion and process units, often interlinked for their feedstock and energy supply;
- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received;
- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements;
- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls are not possible and have to be compensated elsewhere.

This approach consists of considering all concerned emissions together, as emitted through a 'virtual single stack'.

This approach assumes, as a prior condition, that the global result on the environment should be at least as efficient as if BAT-AELs were achieved for every individual process.

Main definition of the concepts used: What is the 'bubble approach' and how could it be applied in a refinery?

Bubble perimeter

The exact bubble perimeter to be considered for a given site will depend on the site processes. For the purpose of this document, this methodology is designed to cover **all sources of permanent emissions from a refinery** (i.e. combustion plants, catalytic crackers, sulphur recovery units, coke calciners and other processes where appropriate), as further indicated.

Bubble substances or parameters covered

Based on the work undertaken in 2009 – 2010 for the revision of this document, SO₂ and NO_x have been recognised as the two parameters which deserve, in priority, a common methodology for a site-level bubble-expressed BAT-AEL calculation, and for which enough supporting information and data have been provided. Therefore, the current methodology will specifically address these two substances.

Bubble averaging period

In the particular context of this document, the methodology proposed has been based primarily on a **yearly average**, since a long-term period has been considered as the most appropriate for reflecting the best performances achievable in normal operating conditions, and giving enough time and flexibility, in order to integrate necessary feedstock, process and fuel adjustments.

However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter-term bubble can, therefore, be derived from the long-term bubble using monitoring results. As real examples of bubble regulations already used by some Member States show, an associated **daily average** could be useful.

Methodology to set a bubble level based on individual BAT-AELs

The site-level bubble is expressed as a sum of two terms:

- **A first term related to the energy system**, including at least all furnaces, stand-alone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable BAT-AEL concentration ranges expected from each category of installation. It includes emissions from internal power plants where energy is exported and excludes emissions from external (out of permit) power plants.
- **A second term related to the process units**, including at least a FCC unit if any, and SRU. This term should be driven by suitable BAT-AEL concentration or specific emission ranges expected from each of them when BAT is applied. It includes emissions from coking: green coke calcination, fluid coking, emissions from SRU (specially SO₂) and PERMANENT emissions from flaring (pilot flames). It excludes emissions from SWS and incondensable untreated gases.

$$\text{Site Bubble} = \frac{\text{Energy system term} + \sum \text{process units terms}}{\text{FL}_{\text{comb}} \times [\text{Comb}] + \text{FL}_{\text{FCC}} \times [\text{FCC}] + \text{FL}_{\text{SRU}} \times [\text{SRU}] + \text{FL}_{\text{other}} \times [\text{other}]}$$

Where: FL= flue-gas
[...] = concentration from process ...

In the context of this document and for the purpose of expressing meaningful BAT-AELs at the site level, the bubble determination should always be based on concentration and specific emission ranges expected from all installations concerned when BAT is applied, and should involve the following steps:

- Step1. Exhaustive identification and geographical mapping of all included sources, to be done according to Appendix A;
- Step2. Determination of the off-gas volumetric contributions expected from all included sources, to be done according to Appendix B;
- Step3. Determination of the mass contributions expected from all included sources, to be done according to Appendix C;
- Step4. Determination of the bubble-associated monitoring regime, to be done according to Appendix D.

8.6.1 APPENDIX A ON 'GOOD PRACTICES' FOR THE IDENTIFICATION AND MAPPING OF ALL INCLUDED SOURCES

Introduction

Reminder of global methodology steps:

- Step1. Exhaustive identification and geographical mapping of all included sources;
- Step2. Determination of the off-gas volumetric contributions expected from all included sources;
- Step3. Determination of the mass contributions expected from all included sources;
- Step4. Determination of the bubble-associated monitoring regime.

The first step of the methodology is crucial as the following steps (calculations) will depend on a clear identification of the sources included in the bubble.

Exhaustive listing of all emitting source (stacks) under the considered bubble area (energy production and processes) including:

- Quick estimation of emission levels for the considered emitted substance (e.g. by using emission factor);
- Prioritising the sources by ranking;
- Listing the currently used monitoring and that required for the corresponding source.

Methods

Refers to existing mapping, e.g. for CO₂ emission trading scheme (ETS), taking into account:

- to include all combustion processes and **identify those using 'non-standard fuels'**;
- to include all refining processes as far as they are in the bubble area;
- to exclude processes that could be on site but are not properly refining, e.g. steam cracker (petrochemical).

Report on map and table all the available operational data (flue-gas volume, load, average or spot concentration measurements, etc.)

References/Examples: CO₂ guidelines document (Decision 2007/589/EC) and EU regulation 601/2012 of 21 June 2012 on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council.

8.6.2 APPENDIX B ON VOLUMETRIC GAS ESTIMATION

Summary of proposed standard flue-gas factors for the bubble calculation

| Source | Fuel or process feed | Flue-gas factor (dry gas) at 3 % O ₂ |
|---|--|--|
| Combustion | Refinery fuel oil (RFO) | 12.3 Nm ³ /kg foe ⁽¹⁾ |
| | Refinery fuel gas (RFG) | 11.3 Nm ³ /kg foe |
| Sulphur recovery unit (SRU) | Acid gas | 1 500 Nm ³ /t feed |
| Fluid catalytic cracking (FCC) | Coke | 12.3 Nm ³ /kg foe |
| Coking process | Green coke calcination | Reported as from 1.8 to 3 Nm ³ per tonne of coke feed |
| | Fluid coking flue-gas | No data |
| Flaring (permanent emissions) | Use combustion emission factor <i>NB: Other than permanent emissions are not included</i> | |
| Sour water stripper (SWS) flue-gas and non-condensables | <i>Not included</i> | |
| ⁽¹⁾ kg foe: kg of fuel oil equivalent = 41.868 MJ (IEA defines tonne of oil equivalent to be equal to 41.868 GJ) <i>Source: [77. REF TWG 2010] [127. France 2010]</i> | | |

Calculation details and general explanations

B.1 FLUE-GAS FLOW RATE - GENERAL

Flue-gas flow rate is rarely measured directly. Where this is the case, the uncertainty in the result of the measurement must be established through a duly documented investigation.

B.1.1 EXPRESSION OF MEASUREMENTS

In all circumstances, the quantity of flue-gases has to be expressed under the same conditions as the other parameters to which they relate.

As far as temperature and pressure conditions are concerned, normal conditions will be systematically used, namely:

- Temperature = 273.15 K or 0 °C
- Pressure = 101 325 Pa or 1 atm.

The normal written form will be used to express these conditions, preceding the unit of volume by the letter N: for example Nm³.

Conversely, the conditions of flue-gas composition in which measurements are expressed will be systematically specified:

- water content: actual content or corrected to 0 % (dry flue-gases);
- oxygen content: actual content or content corrected to a standard value (0 %, 3 % or other value).

Conversion formulae relating to flue-gas composition:

Dry flue-gas flow = wet flue-gas flow x (1 % water in the flue-gas)

*Flow at y % O₂ = flow at x % O₂ * (21-x)/(21-y).*

B.1.2 USING THE RESULTS

Flue-gas flows are used to calculate the quantities of pollutants emitted based on an analysis of flue-gases.

Special care must be taken to ensure that the two terms of the product are expressed using the same units and conditions.

B.2 FLUE-GASES FROM FURNACES AND BOILERS (COMBUSTION)

B.2.1 GENERAL

Flue-gases emitted by these plant items originate from the combustion of fuels and possibly other fluids.

The following rule is to be used for fuels: Flue-gas flow = fuel flow x flue-gas factor

The flow of fuel is to be measured in accordance with the rules described before.

Flue-gas factor represents the quantity of flue-gases produced per unit of fuel.

It is often expressed as Nm³ of dry flue-gas corrected to 3 % O₂ per standard tonne (or tonne of oil equivalent - it is convenient when summing flue-gas volumes generated by different types of fuels (e.g. solid, liquid, gaseous) to express the mass of fuel consumed as tonnes of oil equivalent (toe). The International Energy Agency defines one tonne of oil equivalent (toe) as equal to 41.868 GJ), *as a result of which an approximate fixed factor can be used regardless of what the fuel is.*

The standard flue-gas factor approach is not however sufficiently accurate for complying with the level of uncertainty required by the EU ETS provisions. Statutory obligations for drawing up CO₂ balances have led refineries to obtain a better understanding of the atomic composition of the fuels which they use. The calculations proposed below are based on these characteristics.

B.2.2 FLUE-GAS FACTOR FOR LIQUID FUEL OILS

Liquid fuel oils are analysed on the basis of their compositions by mass:

a % C + b % H + c % S + d % N + e % O

$$\text{QFO flue-gases} = [0.0889 \text{ C \%} + 0.211 \text{ H \%} + 0.0333 \text{ S \%} + (6.8 \times k + 0.8) \text{ N \%} - 0.0263 \text{ O \%}] \times (21/18)/\text{NCVFO}$$

in Nm³/kg of fuel oil equivalent at 3 % O₂ dry gases

With k the proportion of nitrogen which is wholly oxidised.

NCVFO: Net calorific value of fuel oil expressed as MJ/kg

Examples:

For k = 0.2 (typical value)

The fuels in the table have been taken from a Heavy Fuel oils survey and the refinery FO analysed in the context of the CO₂ balance.

| Corrected stoichiometric formula for nitrogen with a nitrogen % oxidised to 20 % NO ₂ (in Nm ³ /kg) | | | | | | | | |
|---|------|------|-----|-----|-----------------------------------|-------------|---|---|
| Vf = 0.0889 C % + 0.211 H % + 0.0333 S % + 0.0216 N % - 0.0263 O % | | | | | | | | |
| | C % | H % | S % | N % | Vf as Nm ³ /kg neutral | NCV as th/t | Vf as Nm ³ /kg at 3 % O ₂ dry gases | Vf as Nm ³ /kg foe at 3 % O ₂ dry gases |
| HF FO survey of LSC | 87.8 | 10.2 | 1.6 | 0.4 | 10.02 | 9 650 | 11.69 | 12.11 |
| HF FO survey of HVF | 86.8 | 10.1 | 2.4 | 0.7 | 9.94 | 9 400 | 11.60 | 12.34 |
| HSC type HVF | 85.5 | 10 | 3.5 | 1 | 9.85 | 9 200 | 11.49 | 12.49 |
| LSC type HVF | 87.5 | 10.5 | 1 | 1 | 10.05 | 9 500 | 11.72 | 12.34 |
| 'LSC' FO | 87.3 | 12 | 0.5 | 0.2 | 10.31 | 9 900 | 12.03 | 12.15 |

HF = Heavy Fuel oil

LSC = Low sulphur content

HSC = high sulphur content

HVF = high viscosity fuel

It will be noted that there is very little variability in the flue-gas factor for liquid fuels.

Analysis of liquid fuels composition is performed 6 to 12 times a year.

Flue-gas factor for the calculation of the bubble (combustion component):

Based on the above, it is proposed to take the typical value of 12.3 Nm³/kg of fuel oil equivalent at 3 % O₂ (dry gases) as a standard flue-gas factor for liquid fuels.

B.2.3 FLUE-GAS FACTOR OF GASEOUS FUELS

FG are analysed on the basis of their mass composition: a HC + b H₂ + c inerts

Hydrocarbons are written as the generic form C_nH_p

Q flue-gases = (a x (4.76n + 0.94p) + b x 1.88 + c) x 22.4 / (a x (12 n + p) + b x 2 + c x 28)
as Nm³/kg

This flue-gas volume is expressed per kg of fuel gas at 0 % O₂ (neutral combustion) on dry gases.

In order to have the factor expressed in Nm³/kg foe, the result has to be divided by the fuel Net Calorific Value.

See the formula above to convert the result at a different O₂ content.

Examples:

The table below also indicates the Net Calorific Values for the various molecules and expresses flue-gas factor (dry gases) in relation to quantity of energy.

| | HC | | | | | | | H ₂ | Inerts |
|--|-----------------|-------------------------------|-------------------------------|--------------------------------|-------------------------------|-------------------------------|-------------------------------|----------------|------------|
| | CH ₄ | C ₂ H ₆ | C ₃ H ₈ | C ₄ H ₁₀ | C ₂ H ₄ | C ₃ H ₆ | C ₄ H ₈ | | |
| n/p | 0.25 | 0.33 | 0.375 | 0.4 | 0.5 | 0.5 | 0.5 | / | / |
| Neutral flue gas factor as Nm ³ /kg | 11.9 | 11.3 | 11.1 | 11.0 | 10.6 | 10.6 | 10.6 | 21.06 | 0.80 |
| Flue gas factor at 3 % O ₂ as Nm ³ /kg | 13.9 | 13.2 | 12.9 | 12.8 | 12.4 | 12.4 | 12.4 | 24.6 | 0.9 |
| NCV (MJ/kg) <i>source: norm NF EN ISO 6976</i> | 50.01 | 47.79 | 46.36 | 45.75 | 47.20 | 46.00 | 45.3 | 120 | 0 |
| NCV as th/t | 11 945 | 11 414 | 11 073 | 10 927 | 11 274 | 10 987 | 10 820 | 28 662 | 0 |
| Flue gas factor at 3 % O ₂ as Nm ³ /kg std | 11.7 | 11.6 | 11.7 | 11.7 | 11.0 | 11.3 | 11.5 | 8.6 | / |

The table below provides values for a typical FG corresponding to the averaging of 700 measurements of different FG with varying composition. The measurements were performed on 12 different units coming from 3 refineries (average of 58 measurements for each unit).

| | % v/v | MM | % m | Dry flue-gas at 3 % O ₂ Nm ³ /kg dry gases | NCV | Dry flue-gas at 3 % O ₂ Nm ³ /kg std dry gases |
|--------------------------------|--------|------|-------|--|-------|--|
| CH ₄ | 25.0 % | 16 | 23 % | 13.92 | 50.01 | 11.65 |
| C ₂ H ₆ | 19.0 % | 30 | 33 % | 13.23 | 47.79 | 11.59 |
| C ₃ H ₈ | 7.0 % | 44 | 18 % | 12.95 | 46.36 | 11.69 |
| C ₄ H ₁₀ | 3.5 % | 58 | 12 % | 12.81 | 45.75 | 11.73 |
| C ₅ H ₁₂ | 1.0 % | 72 | 4 % | 12.70 | 45.35 | 11.72 |
| H ₂ | 40.5 % | 2 | 5 % | 24.57 | 120 | 8.57 |
| N ₂ | 3.5 % | 28 | 6 % | 0.93 | 0 | |
| CO | 0.5 % | 28 | 1 % | 2.47 | 10.11 | 10.23 |
| Total | 100 % | 17.5 | 100 % | 13.02 | 48.07 | 11.34 |

Flue-gas factor for the calculation of the bubble (combustion component):

Based on the above, it is proposed to take the typical value of 11.3 Nm³/kg of fuel oil equivalent at 3 % O₂ (dry gases) as a standard flue-gas factor for gaseous fuels.

B.3 FLUE-GASES FROM SOUR WATER STRIPPER (SWS) GASES

Flue-gases and/or incondensables from SWS gases are not taken into account in the calculation of the flue-gas volume used for determining the bubble.

As it has been considered that such practices cannot be BAT, including such emissions in a permanent bubble calculation could have a counterproductive effect by tolerating them over time and preventing the operator taking drastic actions.

B.4 FLUE-GASES FROM SULPHUR RECOVERY UNITS

The calculations are a simplified formulation based on the flow of acid gas (AG) feeding the unit. The molar composition of acid gas is modelled as three main families, to which ammonia must be added if SWS gases are treated: $a \text{ H}_2\text{S} + b \text{ HC} + c \text{ inerts}$.

Where:

$a = \% \text{ v/v H}_2\text{S}$
 $b = \% \text{ v/v hydrocarbons}$
 $c = \% \text{ v/v inerts}$
 and $a + b + c = 1$

For simplicity, the HC are considered to be C_2H_6 (MM= 30) and the inert components are essentially CO_2 . (MM = 44). These approximations generally have little effect on the result (with a low HC content).

B4.1 MAKE-UP FUEL GAS

Fuel Gas (FG) is injected in the incinerator in order to entirely burn residual H_2S . The flow of FG is represented by the ratio: $j = \% \text{ m of FG to AG}$

B.4.2 ANALYSERS

Gas analysers are mainly:

- H_2S and SO_2 , in the tail gas (TG) downstream of the main reaction zone;
- SO_2 and O_2 in the flue-gas at the exit of the incinerator.

In the following, unless specified otherwise, concentrations are given on dry gases.

B.4.3 CALCULATIONS

Taking into account the actual conversion in the sulphur unit, the molar flow (corresponding to 1 Mol of AG) of the dry residual gas for 0 % O_2 is:

$$f = Q \text{ TG mol} = (1.88a + 15.2b + c)/(1 - 4.76 * \% \text{ SO}_2 \text{ TG} + 0.88 * \% \text{ H}_2\text{S TG})$$

Flue-gas volume exiting the incinerator:

$$Q \text{ incin vol} = (1 + 5.64 * \% \text{ H}_2\text{S TG}) * (1.88a + 15.2b + c)/(1 - 4.76 * \% \text{ SO}_2 \text{tg} + 0.88 * \% \text{ H}_2\text{Stg}) + j * \% \text{ QGA} * 1000 * \text{PF (Nm}^3\text{/h of dry flue-gas at 0 \% O}_2\text{)}$$

Examples:

a) Complete conversion:

| Molar composition | H_2S | HC | Inerts | MM AG | Mol flue-gas/mol AG | Flue-gases $\text{Nm}^3\text{/t AG}$ |
|-------------------|----------------------|-------|--------|-------|---------------------|--------------------------------------|
| Case 1 | 100 % | 0 % | 0 % | 34 | 1.88 | 1 239 |
| Case 2 | 90 % | 0.5 % | 9.5 % | 35 | 1.86 | 1 208 |
| Case 3 | 80 % | 1 % | 19 % | 36 | 1.85 | 1 178 |

In the table above, cases 1 and 3 correspond to extreme values: case 1 would be an AG flux originating from amine treatment of FG, while case 3 would be an AG flux from a FCC, with a high CO₂ content. In practice these fluxes are mixed and case 2 reflects a typical AG composition.

The flue-gas factor increases inversely with the inerts content and in the same direction as HC concentration. In the three situations above, the two parameters partly cancel out and the resulting variability is small.

b) Actual conversion:

Qvol dry flue-gas with combustion of FG in incinerator in Nm³ dry/t AG at 3 % O₂

| Qvol dry flue-gas with combustion of FG in incinerator in Nm ³ dry/t AG at 3 % O ₂ | | | | Composition AG Case 2 | | |
|---|--|--------|--------|-----------------------|--|--------|
| FG=50 % m C ₁ , 50 % m C ₂ | PF (moles dry flue-gas at 3 % O ₂ /g FG) = | 0.52 | MMFG = | 20.87 | Ratio H ₂ S/SO ₂ = | 2 |
| %S [= % v/v SO ₂ % + % v/v H ₂ S]--> | | 0.25 % | 0.50 % | 1.00 % | 2.00 % | 3.00 % |
| Mass ratio FG/GA | | | | | | |
| 0 % | | 1 517 | 1 529 | 1 553 | 1 602 | 1 652 |
| 1 % | | 1 652 | 1 665 | 1 689 | 1 738 | 1 788 |
| 2 % | | 1 788 | 1 800 | 1 825 | 1 874 | 1 923 |
| 3 % | | 1 924 | 1 936 | 1 960 | 2 010 | 2 059 |
| 4 % | | 2 060 | 2 072 | 2 096 | 2 145 | 2 195 |

This method should be used for reporting purposes.

Simplified calculation of flue-gas volume from SRU:

This simplified method allows the flue-gas volume to be expressed with a reduced number of parameters.

Q incin VOL = (2 + 5.76 x %S TG + j % x 18.32) x QGA/MMGA x 22.4 x 10³ x 21/18 (at 3 % O₂ dry gases)

| Qvol dry flue-gas with combustion of FG in incinerator in Nm ³ dry/t AG at 3 % O ₂ | | | Q incin | | |
|---|--------------|--------------|--------------|--------------|--------------|
| %S TG [= % v/v SO ₂ % + % v/v H ₂ S]--> | 0.25 % | 0.50 % | 1.00 % | 2.00 % | 3.00 % |
| Mass ratio FG/AG (j %) | | | | | |
| 0 % | 1 532 | 1 544 | 1 568 | 1 617 | 1 666 |
| 1 % | 1 671 | 1 683 | 1 707 | 1 756 | 1 805 |
| 2 % | 1 810 | 1 822 | 1 847 | 1 895 | 1 944 |
| 3 % | 1 949 | 1 961 | 1 986 | 2 035 | 2 083 |
| 4 % | 2 088 | 2 101 | 2 125 | 2 174 | 2 223 |
| 5 % | 2 227 | 2 240 | 2 264 | 2 313 | 2 362 |
| 6 % | 2 367 | 2 379 | 2 403 | 2 452 | 2 501 |
| 7 % | 2 506 | 2 518 | 2 542 | 2 591 | 2 640 |
| 8 % | 2 645 | 2 657 | 2 682 | 2 730 | 2 779 |
| 9 % | 2 784 | 2 796 | 2 821 | 2 870 | 2 919 |

The table above allows the flue-gas volume emitted by the SRU to be determined as a function of the mass ratio of make-up fuel gas in the incinerator to the acid gas feeding the unit.

The variability of the result is twofold for a given sulphur content in tail gas. However, a typical mass ratio FG/AG of 4 % can be considered as an average value, as it reflects operational constraints (need to ensure an excess of FG to convert residual H₂S), as well as energy efficiency constraints (need to minimise FG consumption as much as possible).

This ratio is very specific to SRU configurations and operating parameters.

B.4.4 FLUE-GAS FACTOR FOR THE CALCULATION OF THE BUBBLE (SRU COMPONENT)

A simplified flue-gas factor which can easily apply to all SRU, regardless of their specificities, has to be established in order to determine the proportion of flue-gas generated by SRU. Such a flue-gas factor should be:

- independent from variable parameters such as the quantity of FG burnt in the incinerator, which anyway is already taken into account in the refinery fuel balance (even if it is a negligible amount, compared to combustion);
- based on available, verifiable, commonly used parameters (such as the quantity of AG feeding the unit and sulphur recovery efficiency).

B.4.5 DETERMINATION OF THE FLUE-GAS VOLUME AS A FUNCTION OF THE SULPHUR RECOVERY EFFICIENCY

By definition the S recovery efficiency is: $\eta = 1 - \%H_2S \text{ unconverted}$

For 1 mole of AG it gives %S incin mol expressed as a function of η :

$$\%S \text{ incin mol} = (100 \% - \eta) \times a / Q \text{ incin mol} \quad (i)$$

$$\%S \text{ incin} = (100 \% - \eta) \times a / (f_0 + 4.76 \times (100 \% - \eta) \times a)$$

$Q \text{ incin vol} = (f_0 + 4.76 \times (100 \% - \eta) \times a) \times 22\,400 / \text{MMGA}$
in Nm³ of dry flue-gas at 0 % O₂/t of AG

With $f_0 = 1.88a + 15.2b + c$

Consider the standard case where:

- $b=1$ (HC in AG = 1 % and HC is C_2H_6)
- make-up FG is CH_4 (PF = $11.93 \text{ Nm}^3/\text{kg}$)
- $f_0 = 1.88a + 0.152 + (100 \% - a - 1 \%) = 0.88 * a + 1.142$

The calculations lead to the following results for the sulphur recovery efficiency.

| Flue-gas volume (Nm^3 at 3 % O_2)/t of AG | | | Sulphur recovery efficiency | | | | |
|---|------|------|-----------------------------|-------|---------|---------|---------|
| | | | MM_{GA} (g) | f_0 | 99.90 % | 99.50 % | 99.00 % |
| H ₂ S content of AG (% v/v) | 99 % | 34.0 | 2.01 | 1 553 | 1 567 | 1 585 | 1 619 |
| | 90 % | 34.9 | 1.93 | 1 453 | 1 466 | 1 481 | 1 511 |
| | 80 % | 35.9 | 1.85 | 1 348 | 1 359 | 1 372 | 1 399 |

B.4.6 STANDARD FLUE-GAS FACTOR FOR THE DETERMINATION OF THE BUBBLE (SRU COMPONENT)

The variability of the previous result is relatively small (less than 15 % for a given recovery efficiency).

It can be shown that even with a 30 % variability on the flue-gas volume from SRUs, the influence on the bubble value is very limited (average standard deviation is 1.3 %).

Based on this, it is proposed to take the typical value of $1\,500 \text{ Nm}^3/\text{t}$ of acid gas at 3 % O_2 (dry gases) as a standard flue-gas factor for SRU.

It corresponds to a H₂S content of 95 % and a sulphur recovery efficiency of 99.5 % but, as mentioned, the variability of the factor is small even when AG composition and efficiency vary.

B.4.7 DETERMINATION OF THE SRU SO₂ EMISSION LEVEL AS A FUNCTION OF SULPHUR RECOVERY EFFICIENCY

Using the same calculations and knowing %S incin, it is possible to determine the SO₂ emission level for SRU expressed as a concentration of SO₂ at the exit of the incinerator (without dilution from the make-up fuel gas).

The SO₂ emission level is then directly related to the recovery efficiency of the unit:

$$[SO_2] = \%S \text{ incin} \times 64/22.4 \times 10^6 \times 18/21$$

Expressed in mg/Nm^3 at 3 % O_2 dry gases

Leading to the following results:

| SO ₂ (mg/Nm^3 at 3 % O_2) incin | | | Sulphur recovery efficiency | | | | |
|---|------|------|-----------------------------|-------|---------|---------|---------|
| | | | MM_{GA} (g) | f_0 | 99.90 % | 99.50 % | 99.00 % |
| H ₂ S content of acid gas (% v/v) | 99 % | 34.0 | 2.01 | 1 201 | 5 952 | 11 768 | 23 009 |
| | 90 % | 34.9 | 1.93 | 1 137 | 5 636 | 11 150 | 21 826 |
| | 80 % | 35.9 | 1.85 | 1 059 | 5 252 | 10 399 | 20 385 |

B.5 FLUE-GAS FLOW FROM THE FCC

The methodology presented below is the most precise and is used within the framework of the ETS reporting. However, it requires a significant amount of data, including measurements which are site- and unit-specific.

This is why a simplified method is presented below, based on a standard flue-gas factor. This latter method will be the one used for determining the flue-gas volume contribution of the FCC unit to the total flue-gas of the refinery for the bubble calculation.

B.5.1 GENERAL CASE

In the catalytic cracking process there is a build-up of coke on the catalyst during the reaction. The coke is burnt in the regenerator, which provides the heat necessary for the reaction and re-establishment of the normal activity of the catalyst.

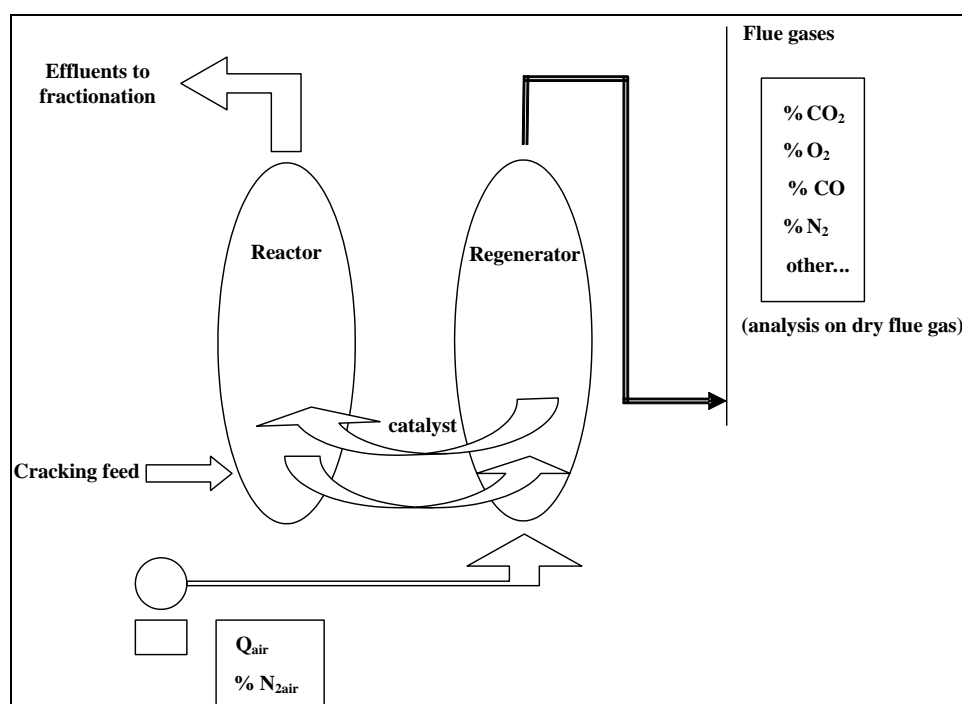


Figure 8.10: Fluid catalytic cracking (FCC) simplified diagram

$Q_{vol\ flue-gases} =$

$$\frac{Q_{mass\ of\ entering\ air} \times 0.79 \times \frac{1}{MM_{dry\ air} + MM_{H_2O} \times \frac{\%water}{1 - \%water}} - Q_{N_2\ mass\ to\ fraction} \times \frac{1}{MM_{N_2}}}{\%N_{2\ flue\ gases}} \times 22.4 \times 1\ 000\ as\ Nm^3/h$$

Where:

$Q_{mass\ entering\ air\ as\ t/h\ moist\ air}$

$MM_{dry\ air} = 28.97\ kg/kMol$

$MM_{H_2O} \times \%water / (1 - \%water) = 0.25\ kg/kMol\ for\ air\ at\ 20\ ^\circ C\ and\ 60\ \% \text{ relative humidity}$

$Q_{N_2\ mass\ to\ fraction\ as\ t/h}$

$MM_{N_2} = 28\ kg/kMol$

Let:

$$Q_{\text{vol flue-gases}} \approx \frac{Q_{\text{mass of entering air}} \times 605 - Q_{\text{N}_2 \text{ mass to fraction}} \times 800}{\%N_{2\text{flue gases}}} \text{ as Nm}^3/\text{h dry flue-gas with the measured O}_2 \text{ content}$$

Note 1: if the atmospheric pollutant analyser is located in a different place from the other analysers involved in the calculation of flue-gas flow, the quantity of gas entering the flue-gas circuit between the 2 measuring points must be added to the calculated flue-gas flow above.

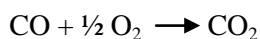
Note 2: the above formula is based on an assumed mean water content corresponding to 60 % relative humidity at 20 °C. The accurate formula is to be preferred, as the corresponding parameters are generally available. Note also that the temperature conditions at the point where the air flow is measured may differ from these for the air sampled.

B.5.2 PARTICULAR CASE OF CO BOILERS

If the atmospheric pollutant analyser is located *on the flow of the boiler output*, the quantity of flue-gases to take into account is the sum of that from the regenerator and that from the combustion of the fuels in the boiler.

The first function (flue-gases from FCC) is calculated as from the above formula by adding the additional flue-gas generation by combustion of the CO in the same way as for the other fuels.

Both functions must be expressed under the same excess air conditions, which shall be taken as nil (that is to say, stoichiometry) to simplify the formulae.



As the volume flow rate of the CO₂ is equal to that of the CO, the additional quantity of flue-gases generated by CO combustion is:

$$Q_{\text{flue-gas CO}} = \text{quantity of nitrogen in air used for combustion of the CO.}$$

Hence:

$$Q_{\text{flue-gas CO}} = \% \text{CO} \times Q_{\text{vol flue-gas}} \times \frac{1}{2} \times \frac{0.79}{0.21} = \% \text{CO} \times Q_{\text{vol flue-gas}} \times 1.88$$

$$Q_{\text{vol flue-gas at 0 \% O}_2} = Q_{\text{vol flue-gas}} \times \frac{21\% - \% \text{O}_2}{21\%}$$

$$Q_{\text{flue-gas CO}} = \% \text{CO} \times Q_{\text{vol flue-gas}} \times 1.88$$

$$Q_{\text{vol flue-gas at 0 \% O}_2} = Q_{\text{vol flue-gas}}$$

%O₂ being the content in O₂ on the regenerator output (measurement point) used in the expression for Q_{vol flue-gas}.

The total volume of flue-gases generated by the FCC, expressed for 0 % O₂ becomes:

$$Q_{\text{total flue-gas}} = Q_{\text{vol flue-gas}} \times \left[\frac{21\% - \% \text{O}_2}{21\%} + \% \text{CO} \times 1.88 \right] \text{ in Nm}^3/\text{h dry flue-gas for 0 \% O}_2$$

B.5.3 FLUE-GAS FACTOR FOR THE CALCULATION OF THE BUBBLE (FCC UNIT COMPONENT)

Coke consumption is an easy-to-obtain variable as its annual consumption in the FCC unit regenerator is reported to the authorities. *It is established on the basis of the methods used for ETS reporting (the coke burnt is deducted from quantities of CO₂ emitted) which offer the best accuracy.*

A benchmark based on 6 FCCs shows very little variability of the flue-gas volume generated by 1 kg of coke as fuel oil equivalent (foe).

Note: The standard flue-gas factor may also be expressed per tonne of feed processed, but the factor will have a larger variability, as the quality of the feedstock can vary significantly.

It is therefore proposed to take the value of 1.2 Nm³/kg of coke (foe) at 3 % O₂ (dry gases) as a standard flue-gas factor for FCC units.

8.6.3 APPENDIX C ON MASS/LOAD EMISSION ESTIMATION

The following tables show the reference values based on individual BAT-AELs to consider when setting a bubble level for the refinery site for SO₂ emissions and NO_x emissions.

Unless stated otherwise, BAT-AELs refer to 3 % oxygen by volume.

Table 8.6: BAT-AEL and BAT-AEPL values for SO₂ emissions

| Source | Type | BAT-AEL/BAT-AEPL Values | Additional information |
|-----------------------------------|------|-------------------------|----------------------------------|
| Combustion | | | See BAT conclusions in Chapter 5 |
| Sulphur recovery unit (SRU) | | | |
| Fluid catalytic cracking (FCC) | | | |
| Calcining of green coke | | {No BAT-AEL} | |
| Flares (permanent emissions only) | | Use combustion BAT-AELs | |

Table 8.7: BAT-AEL and BAT-AEPL values for NO_x emissions

| Source | Type | BAT-AEL/BAT-AEPL Values | Additional information |
|-----------------------------------|------|---|----------------------------------|
| Combustion | | | See BAT conclusions in Chapter 5 |
| Sulphur recovery unit (SRU) | | NO _x emissions considered negligible | |
| Fluid catalytic cracking (FCC) | | | See BAT conclusions in Chapter 5 |
| Calcining of green coke | | {No BAT-AEL} | |
| Flares (permanent emissions only) | | Use combustion BAT-AELs | |

8.6.4 APPENDIX D BUBBLE MONITORING

Setting appropriate monitoring requirements to each stack identified in the mapping

To fully benefit from the existing ETS CO₂ *monitoring plan* to identify the relevant sources and to assess the emissions level (both volumetric and mass contributions) for each substance covered by the bubble.

To define the type of monitoring in accordance with the relevant tier, as for example, following a growing level of emissions:

- use of emission factor and activity parameter monitoring;
- idem previous item and add periodic stack measurements;
- idem first item and add continuous stack measurements.

The following requirements can be associated to the corresponding emissions sources (to be considered alongside the requirements for the monitoring of emissions in Chapter 5):

| Source | Type of monitoring | Observations |
|--------------------------------|---|---|
| Combustion | Continuous direct measurements of SO ₂ or calculation based on S % in fuel Continuous direct measurements of NO _x | Technical provisions on monitoring of IED Annex V may be applicable See also detailed monitoring depending on the capacity (MW) in Section 5.1.4 |
| | Periodic measurements of SO ₂ and NO _x for the smallest sources | |
| Sulphur recovery unit (SRU) | Continuous direct measurements of SO ₂ | Possible calculation from fixed S % recovery and S inlet measurement |
| Fluid catalytic cracking (FCC) | Continuous direct measurements of SO ₂ or calculation based on S % in feed/coke Continuous direct measurements of NO _x | Measurements generally required when using DeSO _x and/or DeNO _x catalysts |
| Coking process | Continuous direct measurements of SO ₂ and NO _x | |
| Flares | Permanent emissions of flares monitored from additional fuel consumption | |

Elaborating a formal monitoring plan

The monitoring plan contains the following contents:

- a description of the process to be monitored;
- a list of emissions sources and source streams to be monitored for each process;
- a description of the calculation-based methodology or measurement-based methodology to be used and the associated level of confidence;
- a description of the measurement systems, and the specification and exact location of the measurement instruments to be used at the emission source, i.e. the points of measurement, frequency of measurements, equipment used, calibration procedures, data collection and storage procedures and the approach for corroborating calculation and the reporting of activity data and emission factors.

GLOSSARY

This glossary is meant to facilitate the understanding of the information contained in this document. The definitions of terms in this glossary are not legal definitions (even if some of them may coincide with definitions given in European legislation), they are meant to help the reader understand some key terms in the context of their use in the specific sector covered by this document.

This glossary is divided up into the following sections:

- I. ISO country codes
- II. Monetary units
- III. Unit prefixes
- IV. Units
- V. Chemical elements
- VI. Chemical formulae commonly used in this document
- VII. Acronyms and technical definitions

I. ISO country codes

| ISO code | Country |
|---|---------------------------------------|
| <i>Member States (°)</i> | |
| AT | Austria |
| BE | Belgium |
| BG | Bulgaria |
| CZ | Czech Republic |
| CY | Cyprus |
| DE | Germany |
| DK | Denmark |
| EE | Estonia |
| EL | Greece |
| ES | Spain |
| FI | Finland |
| FR | France |
| HU | Hungary |
| HR | Croatia |
| IE | Ireland |
| IT | Italy |
| LT | Lithuania |
| LU | Luxembourg |
| LV | Latvia |
| MT | Malta |
| NL | Netherlands |
| PL | Poland |
| PT | Portugal |
| RO | Romania |
| SE | Sweden |
| SI | Slovenia |
| SK | Slovakia |
| UK | United Kingdom |
| <i>Non-member countries</i> | |
| CH | Switzerland |
| MK | Former Yugoslav Republic of Macedonia |
| NO | Norway |
| TR | Turkey |
| US | United States |
| (°) The protocol order of the Member States is based on the alphabetical order of their geographical names in the original language(s). | |

II. Monetary units

| Code ⁽¹⁾ | Country/territory | Currency |
|--|--------------------------|---------------------------|
| <i>Member State currencies</i> | | |
| EUR | Euro area ⁽²⁾ | euro (pl. euros) |
| BGN | Bulgaria | lev (pl. leva) |
| CZK | Czech Republic | Czech koruna (pl. koruny) |
| DKK | Denmark | Danish krone (pl. kroner) |
| GBP | United Kingdom | pound sterling (inv.) |
| HUF | Hungary | forint (inv.) |
| LTL | Lithuania | litas (pl. litai) |
| PLN | Poland | zloty (pl. zlotys) |
| RON | Romania | Romanian leu (pl. lei) |
| SEK | Sweden | krona (pl. kronor) |
| <i>Other currencies</i> | | |
| CHF | Switzerland | Swiss franc |
| JPY | Japan | yen |
| NOK | Norway | Norwegian krone |
| USD | United States | US dollar |
| ⁽¹⁾ ISO 4217 codes. ⁽²⁾ Includes Austria, Belgium, Cyprus, Estonia, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Malta, the Netherlands, Portugal, Slovakia, Slovenia and Spain. | | |

III. Unit prefixes

| Symbol | Prefix | 10 ⁿ | Word | Decimal Number |
|--------|--------|------------------|------------|-------------------|
| T | tera | 10 ¹² | Trillion | 1 000 000 000 000 |
| G | giga | 10 ⁹ | Billion | 1 000 000 000 |
| M | mega | 10 ⁶ | Million | 1 000 000 |
| k | kilo | 10 ³ | Thousand | 1 000 |
| ----- | ----- | 1 | One | 1 |
| c | centi | 10 ⁻² | Hundredth | 0.01 |
| m | milli | 10 ⁻³ | Thousandth | 0.001 |
| μ | micro | 10 ⁻⁶ | Millionth | 0.000 001 |
| n | nano | 10 ⁻⁹ | Billionth | 0.000 000 001 |

IV. Units

| Unit | Unit Name | Measure name (Symbol) | Conversion |
|-----------------|-------------------------------|---|--|
| A | ampere | Electric current | |
| atm | normal atmosphere | Pressure | 1 atm = 101 325 Pa |
| bar | bar | Pressure | 1.013 bar = 100 kPa = 1 atm |
| barg | bar of gauge pressure. | Pressure relative to current atmospheric pressure | |
| bbl | US barrel | Volume | US barrel = 159 litres |
| bpcd | barrels per calendar day | Average flow rates based on operating 365 d/yr | |
| bpsd | barrels per stream day | Flow rates based on actual on-stream time of a unit | |
| Btu | British thermal unit | Energy | 1 Btu ~ 1 054 J 1 TBtu ~ 1.054 million GJ |
| °C | degree Celsius | Temperature | |
| °API | degree API | Density | Specific density = 141.5/(°API+131.5) |
| d | day | Time | |
| dB(A) | decibel | Noise unit A-weighting sound pressure level | |
| FOE | fuel oil equivalent | Energy | 1 tonne FOE = 4.25•10 ¹⁰ J |
| g | gram | Weight | |
| h | hour | Time | |
| ha | hectare | Area | 1 ha = 10 ⁴ m ² |
| Hz | hertz | Frequency | |
| J | joule | Energy | |
| K | Kelvin | Temperature | 0 °C = 273.15 K |
| kcal | kilocalorie | Energy | 1 kcal = 4.186 8 kJ |
| kg | kilogram | Weight | |
| kWh | kilowatt-hour | Energy | 1 kWh = 3 600 kJ |
| l | litre | Volume | |
| m | metre | Length | |
| m ² | square metre | Area | |
| m ³ | cubic metre | Volume | |
| min | minute | Time | |
| MW | megawatts | Energy | |
| Mt/yr | Million of tonnes per year | Throughput annual amount | |
| N | Newton | Force | 1 N= 1 kg m/s ² |
| Nm ³ | normal cubic metre | Volume at 101.325 kPa, 273 K | |
| Pa | pascal | Pressure | 1 Pa = 1 N/m ² |
| ppb | parts per billion | Composition of mixtures | |
| ppm | parts per million | Composition of mixtures | |
| ppmw | parts per million (by weight) | Composition of mixtures | |
| psi | pounds per inch | Pressure | 1 bar = 14.5 psi |
| ppmv | parts per million (by volume) | Composition of mixtures | |
| s | second | Time | |
| sq ft | square foot | Area | 1 sq ft = 0.092 m ² |
| St | stokes | Kinematic viscosity | 1 St = 10 ⁻⁴ m ² /s |
| t | metric tonne | Weight | 1 t = 1 000 kg or 10 ⁶ g |
| t/d | tonnes per day | Materials consumption | |
| t/yr | tonnes per year | Materials consumption | |
| V | volt | Voltage - Electric potential | |
| % v/v | percentage by volume | Composition of mixtures | |
| % w/w | percentage by weight | Composition of mixtures | |
| W | watt | Power | |
| yr | year | Time | |
| Ω | ohm | Electrical resistance | |

V. Chemical elements

| Symbol | Name | Symbol | Name |
|--------|-------------|--------|---------------|
| Ac | Actinium | Mn | Manganese |
| Ag | Silver | Mo | Molybdenum |
| Al | Aluminium | N | Nitrogen |
| Am | Americium | Na | Sodium |
| Ar | Argon | Nb | Niobium |
| As | Arsenic | Nd | Neodymium |
| At | Astatine | Ne | Neon |
| Au | Gold | Ni | Nickel |
| B | Boron | No | Nobelium |
| Ba | Barium | Np | Neptunium |
| Be | Beryllium | O | Oxygen |
| Bi | Bismuth | Os | Osmium |
| Bk | Berkelium | P | Phosphorus |
| Br | Bromine | Pa | Protactinium |
| C | Carbon | Pb | Lead |
| Ca | Calcium | Pd | Palladium |
| Cd | Cadmium | Pm | Promethium |
| Ce | Cerium | Po | Polonium |
| Cf | Californium | Pr | Praseodymium |
| Cl | Chlorine | Pt | Platinum |
| Cm | Curium | Pu | Plutonium |
| Co | Cobalt | Ra | Radium |
| Cr | Chromium | Rb | Rubidium |
| Cs | Caesium | Re | Rhenium |
| Cu | Copper | Rf | Rutherfordium |
| Dy | Dysprosium | Rh | Rhodium |
| Er | Erbium | Rn | Radon |
| Es | Einsteinium | Ru | Ruthenium |
| Eu | Europium | S | Sulphur |
| F | Fluorine | Sb | Antimony |
| Fe | Iron | Sc | Scandium |
| Fm | Fermium | Se | Selenium |
| Fr | Francium | Si | Silicon |
| Ga | Gallium | Sm | Samarium |
| Gd | Gadolinium | Sn | Tin |
| Ge | Germanium | Sr | Strontium |
| H | Hydrogen | Ta | Tantalum |
| He | Helium | Tb | Terbium |
| Hf | Hafnium | Tc | Technetium |
| Hg | Mercury | Te | Tellurium |
| Ho | Holmium | Th | Thorium |
| I | Iodine | Ti | Titanium |
| In | Indium | Tl | Thallium |
| Ir | Iridium | Tm | Thulium |
| K | Potassium | U | Uranium |
| Kr | Krypton | V | Vanadium |
| La | Lanthanum | W | Tungsten |
| Li | Lithium | Xe | Xenon |
| Lr | Lawrencium | Y | Yttrium |
| Lu | Lutetium | Yb | Ytterbium |
| Md | Mendelevium | Zn | Zinc |
| Mg | Magnesium | Zr | Zirconium |

VI. Chemical formulae commonly used in this document

| Chemical formula | Name |
|--------------------------------|--|
| HF | Hydrofluoric acid |
| KOH | Potassium hydroxide. Also called caustic potash |
| H ₂ O ₂ | Hydrogen peroxide |
| H ₂ SO ₄ | Sulphuric acid |
| HCl | Hydrochloric acid |
| MEK | Methyl ethyl ketone |
| MIBK | Methyl isobutyl ketone |
| NaOH | Sodium hydroxide. Also called caustic soda |
| NH ₄ -N | Ammonium (calculated as N) |
| NO ₂ -N | Nitrite (calculated as N) |
| NO ₃ -N | Nitrate (calculated as N) |
| NO _x | The sum of nitric or nitrogen(II) oxide (NO) and nitrogen dioxide (NO ₂) expressed as NO ₂ |
| SO _x | The sum of sulphur dioxide (SO ₂) and sulphur trioxide (SO ₃) expressed as SO ₂ |

VII. Acronyms and technical definitions

A

| | |
|---------------|---|
| Absorption | A volume process in which one substance permeates another (soaking up) |
| AC | Alternating Current |
| AC | Activated Carbon |
| ACC | Annualised capital charge |
| Adsorption | A surface process. The adhesion of molecules of a gas, liquid or dissolved substance to a solid surface resulting in the formation of a thin film on the surface of the solid (surface assimilation) |
| Amylenes | Pentenes |
| AOC | Accidentally Oil Contaminated |
| API | American Petroleum Institute |
| API separator | Oil/water/sludge separator (developed by the American Petroleum Institute) |
| ASU | Activated Sludge Unit |
| Auto-Oil | Co-operative programmes between the EU and the oil and motor industries to find the most cost-effective way to improve air quality in Europe. These have led to Directives on fuel properties and vehicle emissions |

B

| | |
|----------|---|
| BAT-AEL | Emission level associated with the best available techniques |
| BAT-AEPL | Environmental performance level associated with the best available techniques |
| BBU | Bitumen Blowing Unit |
| BFO | Bunker Fuel Oil |
| BFW | Boiler Feed Water to produce steam or hot water |
| Biofuel | Liquid or gaseous fuel for transport produced from biomass |
| BOD | Biochemical Oxygen Demand |
| BREF | Best Available Techniques reference document |
| BTEX | Benzene, Toluene, Ethylbenzene, Xylene |
| BTX | Benzene, Toluene, Xylene |

C

| | |
|----------------|---|
| CAGR | Compound Annual Gross Rate |
| CAS | Chemical abstracts service (registry number) |
| cat cracker | Catalytic cracker (typically refers to fluid catalytic cracker) |
| CCGT | Combined Cycle Gas Turbine |
| CCR | Conradson Carbon Residue (See under Concarbon more information) |
| CDD/CDF | Chlorodibenzoparadioxins/furans |
| CDU | Atmospheric Crude Distillation Unit |
| CEMS | Continuous emissions monitoring system. |
| CHP | Combined Heat and Power (co-generation) |
| CMR | Carcinogenic, mutagenic, reprotoxic |
| COC | Continuously Oil Contaminated |
| COD | Chemical Oxygen Demand |
| Concarbon | Conradson carbon = measurement of carbon residue (expressed in % w/w). Measurement of the tendency of a hydrocarbon to form coke |
| CONCAWE | European Refinery Association for Environment, Health and Safety |
| CORINAIR | European Air Emissions inventory |
| CPI | Corrugated Plated Interceptor |
| C _x | Hydrocarbons with x number of carbons |
| CW | Cooling Water |

D

| | |
|-----|-------------------------|
| DAF | Dissolved Air Flotation |
| DGF | Dissolved Gas Flotation |
| DC | Direct Current |

| | |
|-------------------|---|
| DCU | Delayed Coker Unit |
| DeNO _x | Process/technique for reducing nitrogen oxides from waste gases |
| DeSO _x | Process/technique for reducing sulphur oxides from waste gases |
| DEA | Diethanol Amine |
| DGA | Diglycolamine |
| DIAL | Differential absorption light detection and ranging |
| DIPA | Di-isopropanol amine |
| DNB | Nitrification/denitrification biotreater |
| DS | Dissolved Solids |
| E | |
| EEA | European Environment Agency |
| EEB | European Environmental Bureau |
| EFRT | External Floating Roof Tanks |
| EFTA | European Free Trade Association (established on 3 May 1960) |
| EIA | Environmental Impact Assessment |
| EII | Energy Intensity Index (Solomon index. See Section 3.10.1) |
| EIPPCB | European IPPC Bureau |
| EMAS | European Community Eco-Management and Audit Scheme (EC 1221/2009) |
| EMS | Environmental Management System (see Section 4.15.1) |
| Emissions factor | The estimated average emissions rate of a given pollutant for a given source, relative to units of activity |
| EN | European Norming standard |
| EOP | End-of-pipe |
| EPA | (United States) Environmental Protection Agency (also US EPA) |
| ETBE | Ethyl tert-butyl ether |
| EU | European Union |
| EU-27 | Member States of the European Union on 1 January 2007 |
| EU+ | EU-27 plus Croatia, the Former Yugoslav Republic of Macedonia, Norway, Switzerland and Turkey |
| F | |
| FAME | Fatty acid methyl ester (reference: EN 14214) |
| FBI | Fluidised bed Incinerator |
| FC | Flue Control |
| FCC | Fluidised bed Catalytic Cracking or Fluid Catalytic Cracker |
| FCCU | Fluidised bed Catalytic Cracking Unit or Fluid Catalytic Cracker Unit |
| FF | Fresh feed (used for operating cost e.g. EUR/tonnes FF) |
| FFU | Flocculation/flotation unit |
| FGD | Flue-gas Desulphurisation |
| FGR | Flue-gas Recirculation |
| FID | Flame ionisation detector |
| FOE | Fuel oil equivalent |
| FRT | Fixed roof tank |
| G | |
| GAC | Granular activated carbon |
| GC | Gas Chromatography |
| GCV | Gross calorific value (see also NCV) |
| GO | Gas oil |
| GT | Gas turbine |
| GTCC | Gas turbine combined cycle |
| H | |
| HC (1) | Hydrocarbon |
| HC (2) | Hydrocracking |
| HCU | Hydrocracker Unit |

| | |
|---------------------|---|
| HDM | Hydrodemetallisation |
| HDS | Hydrodesulphurisation |
| HFO | Heavy Fuel Oil |
| HGO | Heavy Gas oil |
| HHV | Higher Heating value (see also LHV) |
| HORC | Heavy Oil and Residue Catalytic cracking |
| HP | High Pressure |
| HSE | Health, Safety and Environment |
| HT | High Temperature |
| HVU | High Vacuum Unit |
| Hydrofiner | Selective hydrocracking |
| I | |
| I-TEQ _{DF} | International toxic equivalent of dioxins/furans |
| IAF | Induced Air Flotation |
| IED | Industrial Emissions Directive (2010/75/EU) |
| IFRT | Internal Floating Roof Tank |
| IGF | Induced Gas Flotation |
| IGCC | Integrated Gasification Combined Cycle |
| IMO | International Maritime Organisation |
| IMPEL | European Union Network for the Implementation and Enforcement of Environmental Law |
| IPPC | Integrated pollution prevention and control |
| ISO | International Organisation for Standardization |
| I-TEQ | International toxicity equivalence (used for PCDD/F) |
| K | |
| kero | kerosene |
| L | |
| LCO | Light Coking Oil |
| LCP | Large Combustion Plant |
| LDAR | Leakage Detection and Repair Programme |
| LGO | Light Gas oil |
| LHV | Lower Heating Value (see also HHV) |
| LP | Low Pressure |
| LPG | Liquefied Petroleum Gas |
| LT | Low Temperature |
| LVGO | Light Vacuum Gas oil |
| LVOC | Large Volume Organic Chemicals |
| M | |
| MAH | Mono Aromatic Hydrocarbon |
| MAH (2) | Major accident and hazard |
| MDEA | Mono diethanolamine |
| MEA | Mono ethanolamine |
| MP | Medium Pressure |
| MS | EU Member State |
| MTBE | Methyl Tert-butyl Ether |
| N | |
| n- | normal, linear organic compound |
| N- | Normal (refers to volume of gases under normal conditions: temperature 0 °C and pressure of 1 atmosphere (101.3 kPa)) |
| NA | Not available (typically for data not available within the document) |
| Naphthenic | The naphthenes contain one or more saturated rings of 5 or 6 carbon atoms in their molecules to which paraffinic-type branches are attached |

| | |
|-------------------|---|
| NCV | Net calorific value or lower heat value (LHV) (see also: GCV) |
| NG | Natural gas |
| NGO | Non-governmental organisation |
| NMVO | Non-methane volatile organic compounds |
| NOC | Non-oil contaminated |
| NO _x | Nitrogen Oxides (NO + NO ₂ , normally expressed as NO ₂) |
| O | |
| OP | Operational costs (fixed or variable) |
| P | |
| PAC | Powdered activated carbon |
| PAH | Polycyclic Aromatic Hydrocarbons |
| PC | Pressure Control |
| PCDD/F | Polychlorodibenzoparadioxins/furans |
| Platformer | Type of catalytic reformer |
| PM | Particulate Matter |
| PM ₁₀ | Particulate matter of size less than 10 µm |
| PM _{2.5} | Particulate matter of size less than 2.5 µm |
| Poly-unit | Polymerisation unit |
| PPI | Parallel Plate Interceptor |
| PPS | Pressurised cross flow plate separation of the desalting unit |
| PSA | Pressure swing adsorption used for purification of hydrogen |
| Pt-based | Used for catalysts containing platinum |
| PUF | Pick-up factors- kg SO ₂ removed per kg additive introduced |
| R | |
| RCC | Residue Catalytic Cracker |
| Residue | The heaviest fractions of the distillation and conversion units. These fractions are used as feedstock in other processes or as liquid refinery fuel |
| RFG | Refinery Fuel Gas |
| RO | Reversed Osmosis |
| RON | Research Octane Number |
| RSH | Mercaptan |
| RVP | Reid Vapour Pressure |
| S | |
| S | Sulphur |
| SCR | Selective Catalytic Reduction |
| SF | Sand Filter |
| SNCR | Selective Non-Catalytic Reduction |
| SO _x | Sulphur oxides (SO ₂ and SO ₃) |
| SRA | Sulphur reduction additives |
| SRU | Sulphur Recovery Unit |
| SS | Suspended Solids |
| SW | Sour Water |
| SWS | Sour Water Stripper |
| T | |
| TAME | Tertiary Amyl Methyl Ether |
| TCDD/F | Tetrachlorodibenzoparadioxins/furans (toxicity reference for dioxins) |
| TEC | Total erected cost |
| TEL | Tetra ethyl lead |
| TKN | Total Kjeldahl nitrogen - the sum of organic nitrogen, ammonia (NH ₃) and ammonium (NH ₄ ⁺) in the chemical analysis of soil, water, or waste water. |
| TGT | Tail Gas Treatment of the sulphur recovery unit |
| TML | Tetra methyl lead |

Glossary

| | |
|-------------|---|
| TN | Total nitrogen – the sum of total Kjeldahl nitrogen and nitrate and nitrite |
| TOC | Total Organic Carbon |
| TSS | Total Suspended Solids (water) |
| TSS (2) | Third-stage separator (air) |
| TWG | European Technical Working Group on refineries |
| U | |
| U | Unit (used together with names of process) |
| UF | Ultrafiltration |
| Ultraformer | Type of reformer |
| US EPA | Environmental Protection Agency of the United States |
| V | |
| V. I. | Viscosity Index |
| VBU | Visbreaking Unit |
| VGO | Vacuum gas oil |
| VOC | Volatile Organic Compound |
| VR | Vacuum Residue |
| VRO | Vacuum residue oil |
| VRU | Vapour Recovery Unit |
| VSBO | Visbreaking Gas oil |
| W | |
| WGS | Wet gas scrubber |
| WHB | Waste Heat Boiler |
| WWTP | Waste Water Treatment Plant |
| Z | |
| Zeolites | Microporous, aluminosilicate minerals commonly used as molecular sieves. |

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