Faculty of Chemical Engineering and Technology
University of Zagreb

Petroleum Refining and Petrochemical Processes

Natural Gas

Composition, Classification, Processing

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ZAVOD ZA TEHNOLOGIJU NAFTE I PETROKEMIJU
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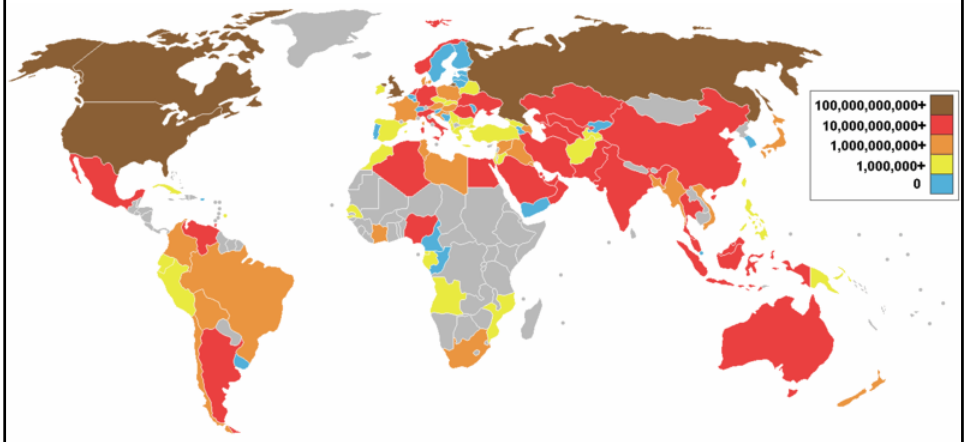
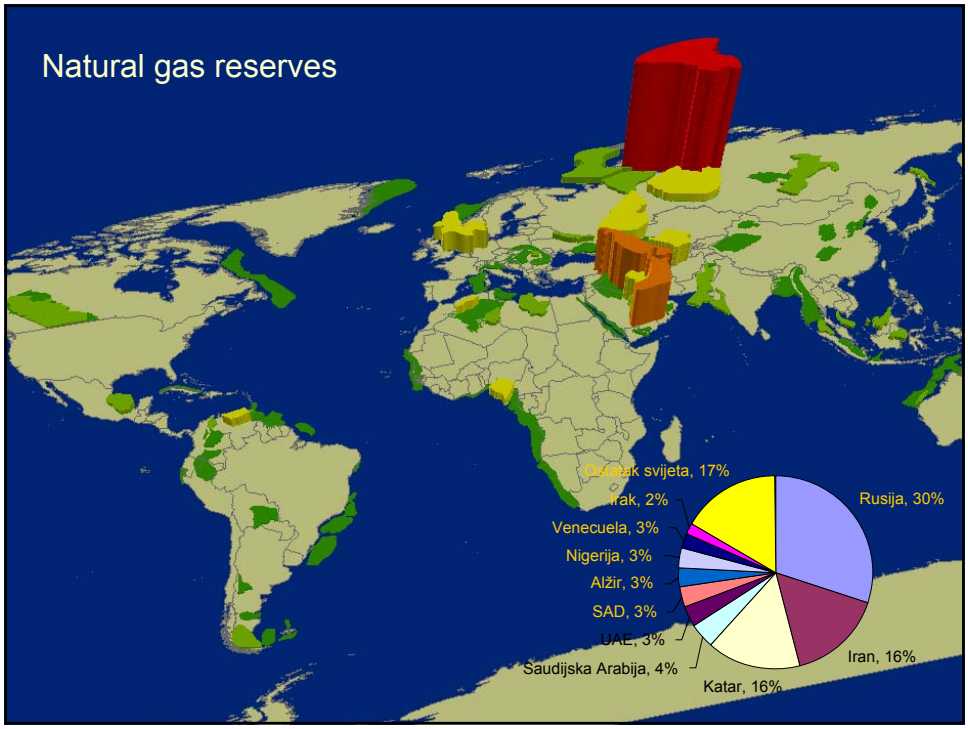
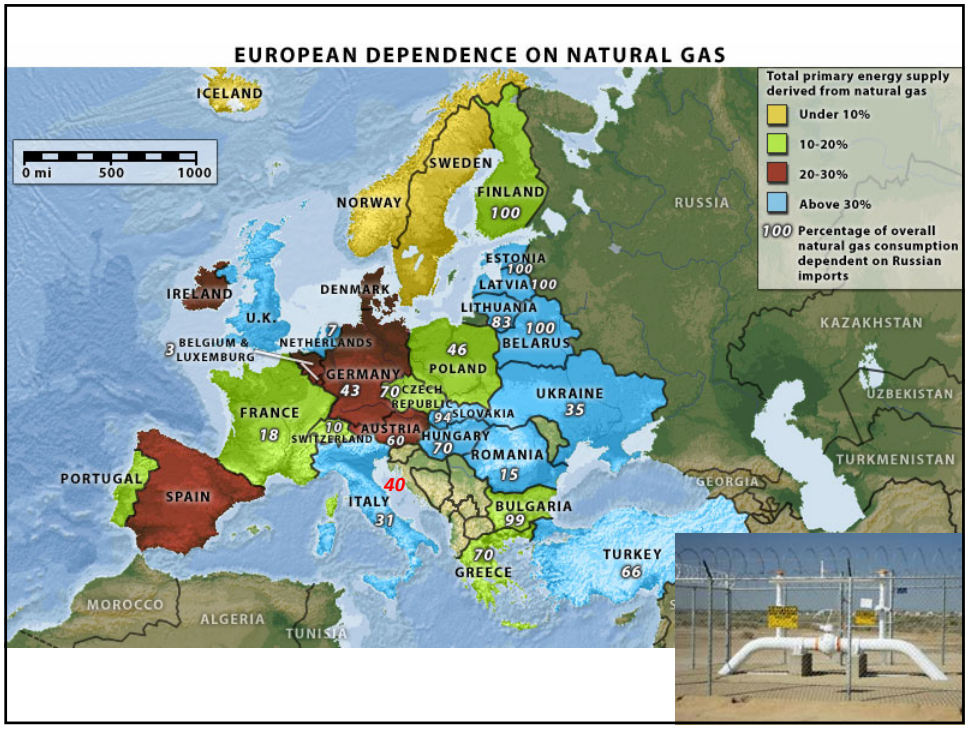
Natural gas – naturally occurring mixture of saturated light hydrocarbons consisting primarily of **methane**, **CH_4** (> 70 %), accompanied by some non-hydrocarbon compounds:
carbon dioxide, nitrogen and hydrogen sulfide (*CO_2 / N_2 / H_2S)*

Natural gas is an energy source often used for heating, cooking (town gas), and electricity generation. It is also used as fuel for vehicles and as a chemical feedstock in the manufacture of plastics and other commercially important organic chemicals (syn-gas, hydrogen, ammonia, methanol...).

Natural gas extraction by countries in cubic meters (Nm^3) per year







Tipical composition of natural gas:

hydrocarbons: CH_4 > 70 %, C_2 < 15 %, C_3 < 9 %, C_4 < 4 %, C_{5+} < 2 %
non-hydrocarbons / impurities: CO_2, H_2S, COS, H_2O, N_2 , …
noble gases He, Ar, Ne, … up to 0.1 %, Hg rarely.

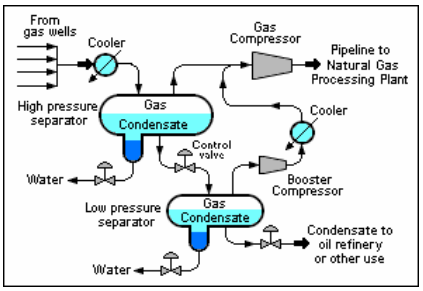
According to heavier hydrocarbon content in natural gas:

a) dry gas: C_{4+} < 15 mg kg^{-1} (ppm)
b) wet gas: C_{4+} > 40 mg kg^{-1}
c) sour gas (high content of acidic gases): CO_2 > 3 % and H_2S > 7 mg kg^{-1}

Natural gas:

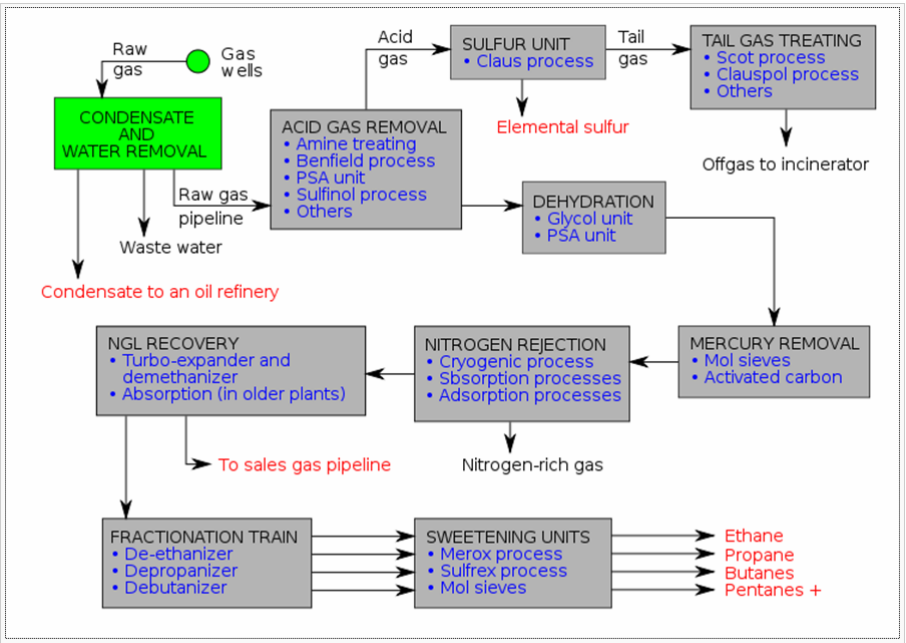
1) "associated" - found in oil fields,
*2) "non-associated" - isolated in natural gas fields (*95 % share in reserves)

Natural-gas condensate is a low-density mixture of hydrocarbon liquids (C_5··· C_{30}) *that are present as gaseous components in the raw natural gas produced from many natural gas fields.*
It condenses out of the raw gas if the temperature is reduced to below the hydrocarbon dew point temperature of the raw gas.
The natural gas condensate is also referred to as simply condensate, or gas condensate, or sometimes natural gasoline because it contains hydrocarbons within the gasoline boiling range.



Composition / vol. %	*non-associated natural gas / geological source*			
	Molve	**Kalinovac**	**Algeria**	**Texas**
CH_4	70,0	75,0	83,0	76,2
C_2H_6	3,5	7,0	7,2	6,4
C_3H_8	2,0	3,5	2,3	3,8
C_{4+}	1,2	1,7	1,3	3,1
CO_2	23,0	12,5	0,2	0,2
H_2S / mg kg^{-1}	65,0	80,0		
Hg / mg m^{-3}		0,1···1,0		
H_2O / g m^{-3}		30···45		

C_{4+} butane (C_4H_{10}) and heavier HC (hydrocarbons)



Schematic flow diagram of a typical natural gas processing plant.

NATURAL GAS PROCESSING

A. Removal of acid gases (CO_2, H_2S, COS) and traces of mercury

Acid gases are undesirable because they are mostly toxic and corrosive:

CO_2 – reduces the heat of combustion, under conditions of high pressure and low temperature exists in the solid state.

H_2S – toxic, corrosive, COS (carbonyl sulfide) - toxic

Hg – highly toxic, although present in small proportions, it must be completely removed

Hg is removed by passage of the gas through special filters filled with sulfur-impregnated activated carbon (15 % S).
This leads to formation of stable mercury sulfide which is occasionaly removed from the filtration device together with the adsorbens.

$$\underset{5\ \mu g\ m^{-3}}{Hg} \xrightarrow{S\ /\ act.\ C} HgS + \underset{< 0.01\ \mu g\ m^{-3}}{Hg\ (residual)}$$

NATURAL GAS PROCESSING

B. Conversion of hydrogen sulfide, H_2S into elemental sulfur, S

C. Water (H_2O) removal

Presence of H_2O in natural gas during processing is also undesirable because of its corrosive effects and its ability to create solid hydrates under high pressure and low temperature ($CH_4 \cdot 6\ H_2O$).
These hydrates are undesirable because they hinder transport and storage.

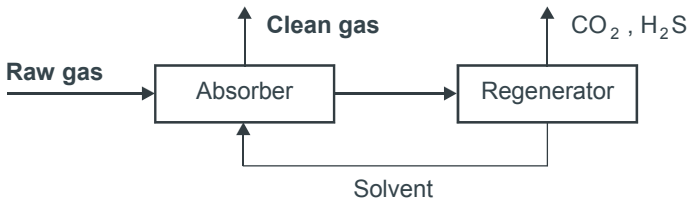
D. Separation of methane from higher hydrocarbons, C_{2+}

Heavier hydrocarbons are being used as separate raw materials: ethane, propane/butane, pentane...

A. ACID GAS REMOVAL

1. **Absorption with chemically active solvents**
2. **Absorption with physically active solvents**
3. **Adsorption with solid adsorbent**

The processes of absorption with solvents are performed in columns with 20 to 25 plates or in columns filled with stacked beds, in counter-current flow, under certain temperature and pressure conditions.



Adsorption processes are also performed in columns and the solid adsorbent is regenerated by heating.

A1. Absorption processes with chemically active solvents

(Chemical Solvent Process)

Solvent reacts with acid gases in reversible or irreversible reaction at low temperatures and is regenerated by releasing the absorbed components at higher temperatures.

The most significant solvents (their aqueous solution) for this proces are:

- potassium carbonate (aq), so-called Benfield process
- sodium hydroxide (aq)
- amines: monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA), diglycolamine (DGA)

A1. Absorption processes with chemically active solvents

A1-1. Benfield process

The process is described as reversible chemical reaction of acid gases with aqueous solution of potassium carbonate.
Regeneration of saturated solution is performed by desorbtion.
This method is commonly used when of CO_2 is present in natural gas in higher share.

The process comprises of counter-current gas scrubbing in columns with aqueous solution of K_2CO_3 (5···10 %), at temperature of ~ 20 °C, and pressure of 20···70 bar.

Regeneration of saturated solution is done by heating, commonly by water vapor (steam) at room pressure:

$$K_2CO_3 + CO_2 + H_2O \quad = \quad 2\ KHCO_3$$

absorption: 20 bar, 20 °C desorption: 1 bar, 105 °C

A1. Absorption processes with chemically active solvents

A1-2. Sodium hydroxide

Acid gas removal process with aqueous solution of sodium hydroxide is an irreversible reaction:

$2\ NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

$2\ NaOH + H_2S \longrightarrow Na_2S + 2\ H_2O$

The proces is performed in series of several counter-current scrubbers with gradually increasing concentration of NaOH, and with H_2O at the end (neutralization).
- pressure and temperature conditions:~ 15 bar, 45 ^oC

sour gas → 0,5 % NaOH → 3 % NaOH → 10 % NaOH → H_2O → **clean gas**

Mercaptans are commonly removed by separate proceess, usually by oxidation with air, in aqueous solution of sodium hydroxide (*Merox process*) with cobalt salts as catalyst (formation of insoluble disulfides)

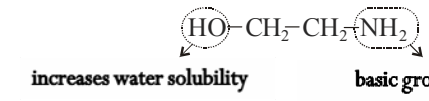
$R–SH \xrightarrow{O_2,\ kat.} R\text{-}S\text{-}S\text{-}R + H_2O$

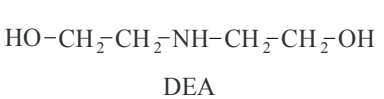
A1. The absorption processes with chemically active solvents

A1-3. Amine solutions

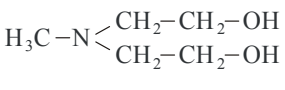
Certain amines, especially ethanolamines, have a high absorption capacity for acid gases (CO_2 and H_2S) and small capacity for hydrocarbons and other impurities. Very often the amine process is used for so-called secondary separations of residual CO_2 after other processes such as Benfield carbonate process (this process separates residual CO_2 to a concentration less than 500 mg kg^{-1} and H_2S to several mg kg^{-1}).

Most effective amines:
monoethanolamine (MEA), diethanolamine (DEA) i methyldiethanolamine (**MDEA**) in the form of an aqueous solutions (15···20 %).





DEA



MDEA

Reactions:

$$HO\text{-}CH_2CH_2\text{-}NH_2 + \mathbf{H_2S} = HO\text{-}CH_2CH_2\text{-}NH_3\cdot SH$$

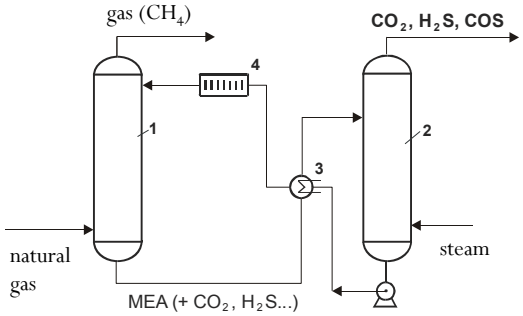
$$2\ HO\text{-}CH_2CH_2NH_2 + \mathbf{CO_2} = HO\text{-}CH_2CH_2\text{-}NH\text{-}CO\text{-}O \cdot NH_3\text{-}CH_2CH_2OH$$

Both reactions are reversible and the equilibrium depends on the temperature and partial pressure (CO_2 and H_2S) in the solution.

Absorption occurs during a chemical reaction (amine and acid gas) at low temperatures (~ 20 °C), with the formation of weak salts;
desorption occurs with weak salts decomposition at high temperatures (> 80 °C).

Mostly it is used 15···20 % aqueous solution of MEA, because then the highest efficiency of absorption and minimum corrosion of the plant.

Scheme of the removal procedure of acid gases from natural gas with MEA aqueous solution



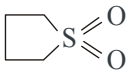
1 – absorber, 2 – regenerator, 3 – heat exchanger, 4 – cooler

The purified gas (CH_4) is separated at the top of the column and amino solution with absorbed acid gases is drained away to the regeneration column. The regeneration column has a similar design like the absorption column and there solution is heated usually with superheated steam to 130 °C at 0.3···1.0 bar.
From the top of the column desorbed gases are removed.
Amine solution is first cooled by heat exchanger (with a solution from absorber), followed by with cold water (which flow through the cooler) and then redosed into the reactor.

A2. The absorption process
Physical Solvent Process (engl. Physical Solvent Process)

Acid gases are selectively absorbed from gas mixtures and then released from solvent by heating.

The most significant solvent:

- dimethylether polyethyleneglycol (Selexol process)
- propylene carbonate
- mixture of sulfolane and DEA (Sulfinol process) (*sulfolane*, )
- methanol (under pressure) (Rectisol, process of the company Lurgi, Germany)

A3. The adsorption processes with solid phase adsorbents

The most significant adsorbents:

zeolites – molecular sieves

activated carbon

(also called activated charcoal, activated coal or carbo activatus)

Fe – dust (iron dust)

zinc oxide

B. Oxidation of hydrogen sulfide

Carbon dioxide and hydrogen sulfide separated from acid gas, with amine of some other procedures are taken to the plant, where the oxidation of H_2S to elementar sulfur is carried out, while carbon dioxide is usually discharged into the atmospere.

Two most important procedures are *Claus* and *chelating process*.

B1. Claus procedure

(1) $H_2S + 1{,}5\ O_2 \rightarrow SO_2 + H_2O$
(2) $SO_2 + 2\ H_2S \rightarrow 3S + 2\ H_2O$
(Σ) $3\ H_2S + 1{,}5\ O_2 \rightarrow 3S + 3\ H_2O$

Process is carried out in two stages:
(1) hydrogen sulfide combustion in the Claus furnance,
(2) by catalyst Al_2O_3 conversion higher than 98 % can be achieved.

The Claus process is mostly use for the oxidation of hydrogen sulfide in the process of hydrodesulfurization and hydrotreating of petroelum products.

B2. Chelation process

- Very effective, oxidation occurs in one reaction
(LO-CAT® proces, ARI Technologies Inc., SAD).

H_2S is oxidized to elemental sulfur in an aqueous medium with a catalyst of Fe-chelate:

$$\mathbf{H_2S + 2\ (Fe\text{-}kelat)^{3+} \longrightarrow 2\ H^+ + 2\ (Fe\text{-}kelat)^{2+} + S^o}$$

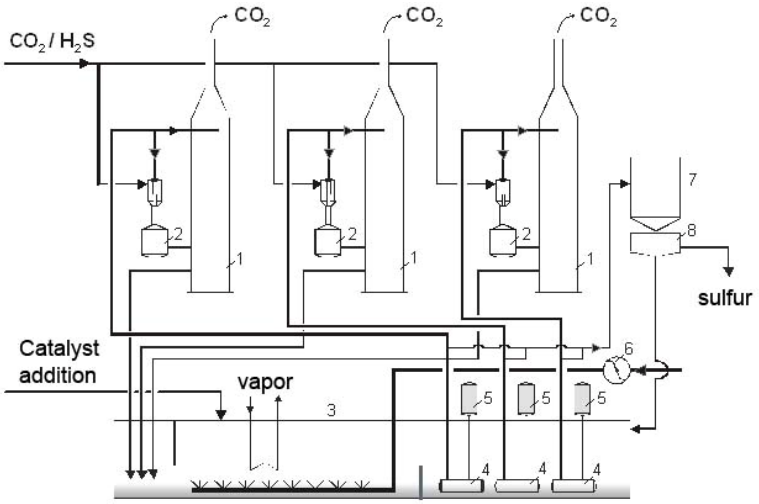
Catalyst is being recovered using oxidation process with air:

$$\mathbf{2\ (Fe\text{-}kelat)^{2+} + ½\ O_2 + H_2O \longrightarrow 2\ (Fe\text{-}kelat)^{3+} + 2\ OH^-}$$

Benefits of chelation process are complete conversion of H_2S to sulfur and easy recovery of catalyst

Process
The process is carried out in two stages:
a) oxidation ($S^{2-} \rightarrow S^o$), b) catalyst recovery($Fe^{2+} \rightarrow Fe^{3+}$).

Gas mixture is metered into the reactor (usually three reactors) by Venturi pump and countercurrent washed with stream of aqueous catalyst. The reactor is filled with stainless steel rings. H_2S reacts chemically and lags behind in the solution and separated CO_2 is released into the atmosphere. The aqueous solution with dispersed sulfur is conducted into the catalyst oxidizer and sulfur precipitator. Sulfur is separated by filtration and the aqueous solution of recovered catalyst is conducted back into the reactor.



Scheme of the oxidation process of sulfide from waste gases

1 - absorber, 2 - Venturi pump, 3 - oxidation chamber, 4 – unit for separation of elemental sulfur, 5 - Pump, 6 - air compressor 7 – sulfur precipitator, 8 - filter

The highest values of hazardous constituents in the waste gases of combustion processes are specified by the law of ecological standards (ISO 14000) .

A maximum allowable concentration of pollutants in waste gases:

Substance	**Concentration / mg m^{-3}**	**Substance**	**Concentration / mg m^{-3}**
H_2S	5	CO_2	without restraint
SO_2	500	Hg	1

C. Water removal

Water in the natural gas is undesirable for several reasons:
(a) cause the increase in corrosion effect
(b) at higher pressures (in pipelines) with hydrocarbons creates solid complexes, hydrates $C_nH_m \cdot H_2O$ (eg $CH_4 \cdot 6\ H_2O$) - this can cause difficulties during their transport through pipelines.

Water (moisture) removal from gas mixtures:

C1. Process with liquid absorbent (washing)

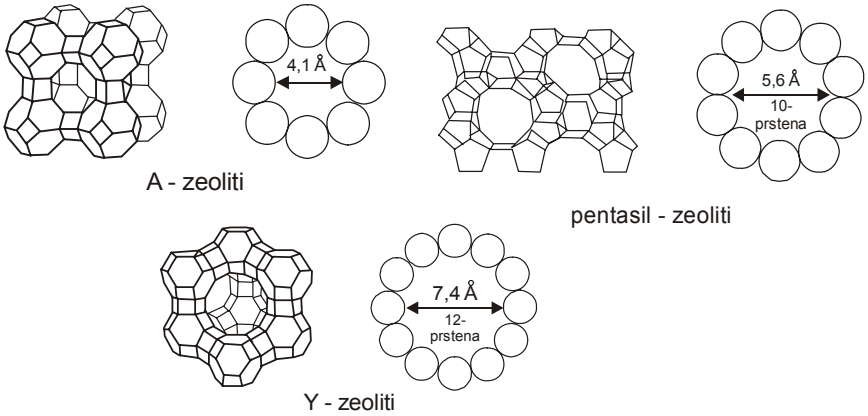
Method for larger amounts of moisture. Glycols are mainly used, usually: HO–CH_2CH_2–OH ethylene-glycol, HO–CH_2CH_2–O–CH_2CH_2–OH diethylene-glycol (DEG) and triethylene-glycol (TEG). Higher glycols have higher boiling point and therefore a lower vapor pressure, but with a smaller absorption effect. The procedure is performed in a countercurrent columns with trays or trickle bodies.

C2. Process with solid absorbent (drying)

Mainly used absorbents:
zeolite - molecular sieves, aluminum oxide and silica gel.

Molecular sieves are synthetic crystalline materials with pore size of 0.4 · · · 1.2 nm.

Structure of Zeolites



General formula:

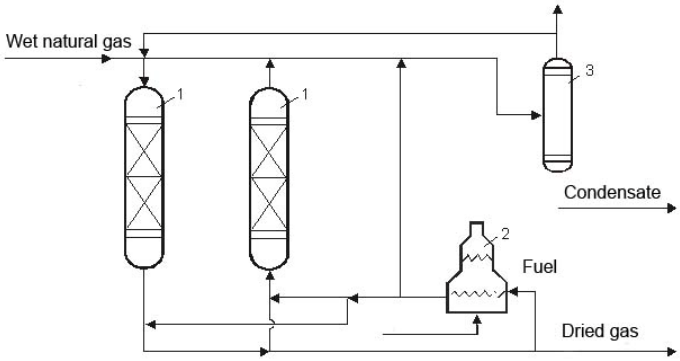
$$(Me_1\ Me_2)\ O \cdot Al_2O_3 \cdot n\ SiO_2$$

Me_1 = Y, Ln, Ce, Me_2 = Na, K, Mg, Ca i n = 2···12

High porosity and surface area: 800···1000 $m^2\ g^{-1}$ - high adsorption capacity.

Drying with molecular sieves - at least two columns filled with granular adsorbent – the duty cycle of adsorption and desorption are alternately repeated (8 + 8 hours).

Wet gas flows from the top to the bottom of the adsorption column and after separation of moisture (up to 0.05 mg kg-1) leads to the tank. Part of the dry gas is heated by passing through a special tube furnace (up to 300 °C), then passes through the recovery column and washing the adsorbent from the bottom to the top of the column, it cools, leaving the condensed water separator and joins wet gas.



Drying plant scheme of natural gas with molecular sieves
1 - dryer, 2 - furnace, 3 – water condensate separator

Advantages of molecular sieves for drying gases:

- high efficiency of drying (< 0.05 mg kg^{-1} moisture)
- high temperature regeneration of adsorbent
- quick recovery (8 h of adsorption, desorption 8 hours)
- high durability
- beside water removal they are used for adsorption: H_2S, RSH, COS.

The main disadvantage is their relatively high cost.

D. Separation of higher hydrocarbons

Natural gas (composed mostly of higher hydrocarbons) is processed and higher hydrocarbons are separated from methane by specific procedures.
Products of mentioned processes, beside methane, are: ethane, propane, n-butane, isobutane and C_{5+} (pentane and higher hydrocarbons).

Usage of separated hydrocarbons:

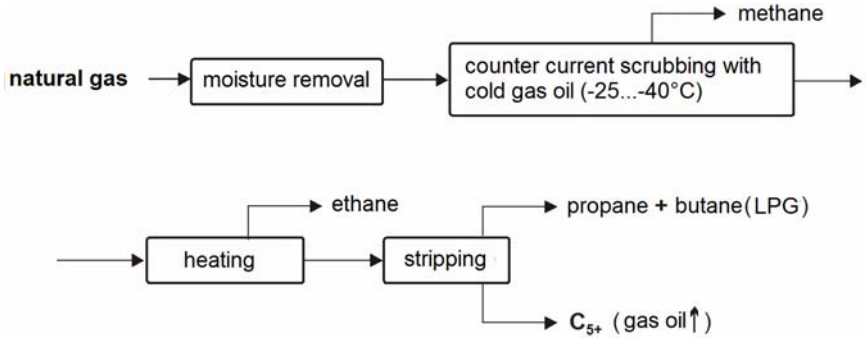
- ethane is basic chemical in production of ethylene
- mixture of *propane / butane*, at standard conditions is in gaseous state, but at elevated pressures is a liquid known as *Liquefied Petroleum Gas*, LPG.
- heavier hydrocarbons C_{5+}, "natural gasoline" (stabilized gasoline), is added to motor gasoline as one of the compounds.

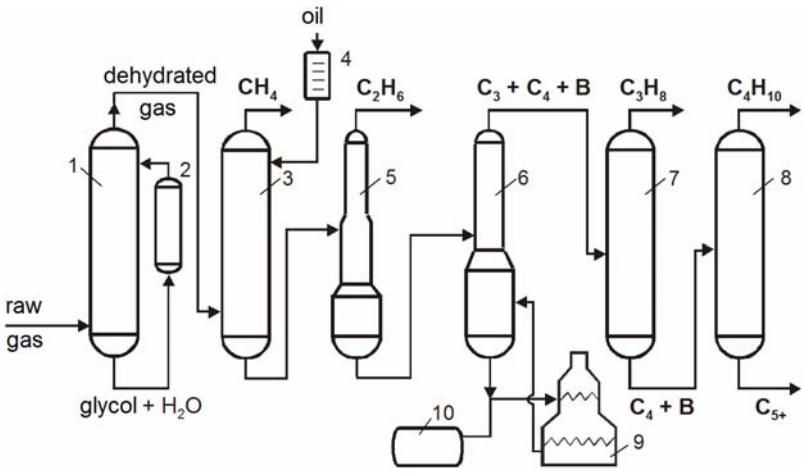
Procedures of extractions of mentioned alkanes from natural gas:

1) **absorption**, 2) **expansion**.

D1. Absorption procedure

Older than expansion procedure, it is based on absorption of natural gas compounds. Natural gas prior to absorption is cleared from acid gases, absorbs in gas oil (oil fraction with boiling point of 220-360 °C) under low temperatures, followed by its gradual separation by distillation procedures.





Scheme of absorption procedure for separating higher hydrocarbons

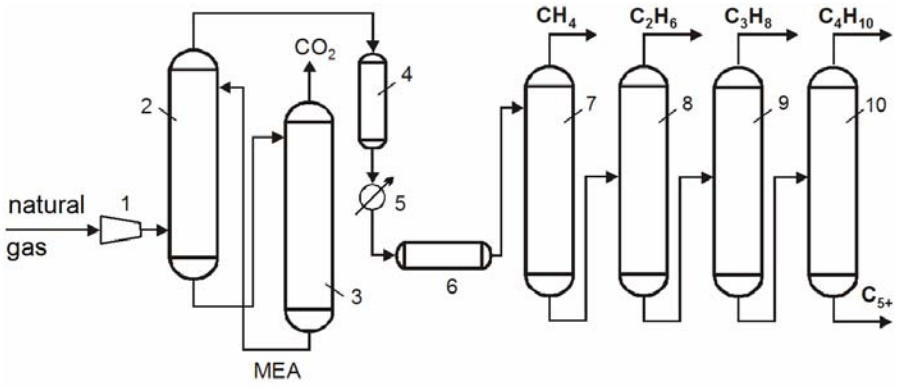
1 – dehydration column, 2 – glycol regenerator, 3 – absorber and demethanizer (separation of methane) 4 – oil cooler, 5 – deethanizer (ethane removal) 6 – oil separation column, 7 - depropanizer (removal of propane), 8 - debutanizer (removal of butane), 9 - furnace, 10 – oil container, C3 – propane fraction, C4 – butane fraction, B – gasoline

D2. Expansion procedure

It is based on separation previously liquefied higher hydrocarbon, the gas is cooled by adiabatic expansion.
Process begins with the removal of acid gases and moisture:

Composition	C_1	C_2	C_3	C_4	C_{5+}	CO_2	N_2
Volume fraction %	85,4	6,8	2,9	1,5	0,7	1,6	1,1

Gas is compressed to 40 bar, and then cooled by liquid propane (-40 °C) over heat exchangers and then is expanded to 10 bar. During the expansion gas is cooled to around -100 °C . Methane is then separated (demethanation), and other condensed compounds are separated by gradual decrease of the pressure 30 - >17 -> 6 bar. Separated fractions are: ethane, propane, butane and C5+ (light gasolin).

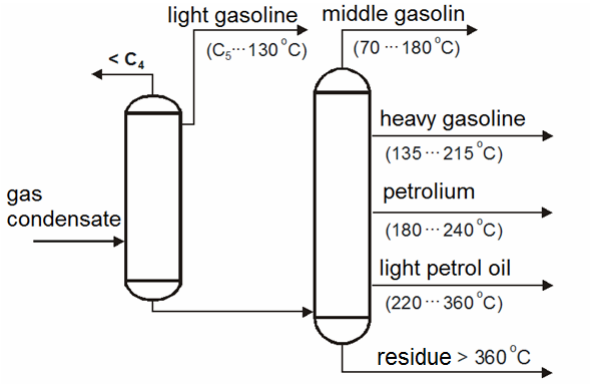


Expansion procedure for fraction separation of natural gas

1 – compressor, 2 – absorption column (CO_2), 3 – regenerator MEA,
4 – absorption H_2O, 5 – cooling device(-60 °C), 6 – expander,
7 – distillation column (methane), 8 – distillation column (ethane),
9 – distillation column (propane), 10 –distillation column (butane)

Gas condensate

Gas condensate is a mixture of hydrocarbons containing around 5-30 C-atoms, is a byproduct of natural gas processing from gas-condensate deposits.
Lower fractions, containing to 10 C-atoms are often called raw gasoline, are part of natural gas. Natural gas from Pannonia pool has the weight fraction of condensate to 22 %. After the separation of lighter hydrocarbons (mostly methane by the procedure called „stabilization"), condensate is processed by atmospheric fraction distillation.

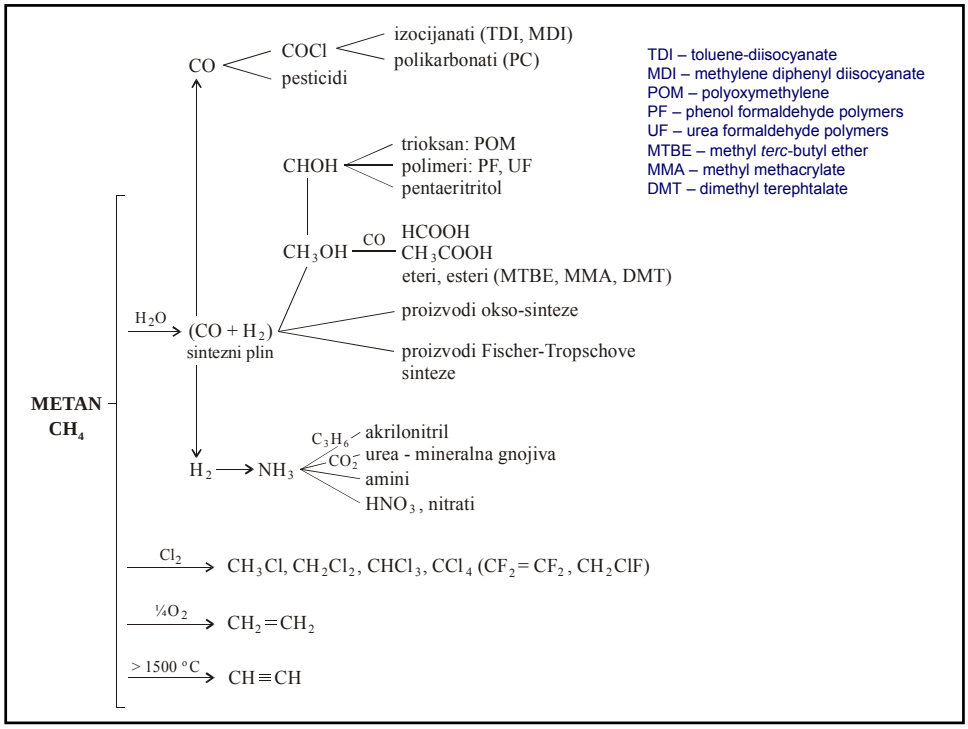


Atmospheric distillation of gas condensate

Natural-gas condensate contains significantly higher content of light fractions compared to crude oil. Most frequently it is used as a petrochemical feedstock, or fractions obtained after the distillation are used as fuel products.

Comparision of composition of gas condensate and crude oil

Composition	Gas condensate	Oil	
	Podravina	Moslavina	Slavonija
Density / g cm^{-3}	0.790	0.860	0.870
S / mass share, %	0.04	0.41	0.47
Benzine / gasoline up to 170 °C	40	25	14
Gasoil, 175···310 °C	35	26	11
Residue (fuel oil), > 310 °C	25	49	75



Liquefied Natural Gas (LNG)

It is obtained by liquefaction of very clean natural gas by expanding process (100 bar → 4 bar) or by direct cooling (in the liquid state, t_v = - 161 °C), with the purpose of transporting of natural gas to long distances, usually by special ships.

Common transport routes are:
from Alaska to other parts of the United States, from Algeria and other Middle East countries to Western Europe and Japan.

1 m^3 of liquefied natural gas = 600 Nm^3 of gas

LNG composition: **methane**, at least 90 % up to 100 %;
may contain ethane, propane and higher CH.
Liquefaction process removes O_2, CO_2, H_2O, S-compounds.

LNG density: about 45 % of the density of water.
Odorless, colorless, non-corrosive, non-toxic.
Vapor at concentrations of 5 – 15 % in the air mixture can burn.
Neither LNG, nor its vapors are explosive in the open air.

Straits Times, January 18 - 2011

Liquid Petroleum Gas (LPG)

- a mixture of **propane and butane** in various proportions, can include propylene, butylene, and iso-butane.

Composition is often adjusted to seasonal conditions - in winter, higher proportions of propane, in summer butane.
Vapour pressure at 30 °C, for commercial propane from 10-12 barg, commercial butane, 2-4 barg.

LPG compared with natural gas has a much lower heat value and requires a different ratio of the air-gas (propane, 24:1; butane, 30:1) for good combustion.

It is stored as a liquid under pressure in tanks.
Does not require expensive investments in infrastructure as LNG, and is widely applicable in developing countries (India) and rural areas.

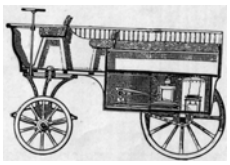
LPG is often referred to as *auto gas* when used as a fuel for vehicles.

Compressed natural gas (CNG)

- Natural gas compressed at pressures up to 3,600 psig; is stored in suitable tanks.

Usually its composition matches to that of the local gas pipeline, with a little water removed. It is provided to the motor as a low-pressure gas (300 psig).

CNG may be obtained from LNG, at a lower cost.



First viecle powered by natural gas, 1860.

Pounds of Air Pollutants Produced per Billion Btu of Energy

Pollutant	Natural Gas	Oil	Coal
Carbon Dioxide, CO_2	117 000	164 000	208 000
Carbon Monoxide, CO	40	33	208
Nitrogen Oxides, NO_x	92	448	457
Sulfur Dioxide, SO_2	1	1 122	2 591
Particulates	7	84	2 744
Mercury, Hg	0.000	0.007	0.016

Source: EIA - Natural Gas Issues and Trends 1998.