University of Diyala

Faculty of Engineering

Chemical Engineering Department

Fourth Year

Natural Gas Processing

2021

Recommended Books:

1. Saeid Mokhatab, William A.Poe and James G.Speight. "Hand book of Natural Gas Transmission and Processing" 2006.
2. Arthur J. Kidnay & William R. Parrish “Fundamentals of Natural Gas Processing” 2006.
3. Xiuli Wang XGAS “Advanced Natural Gas Engineering” 2009.

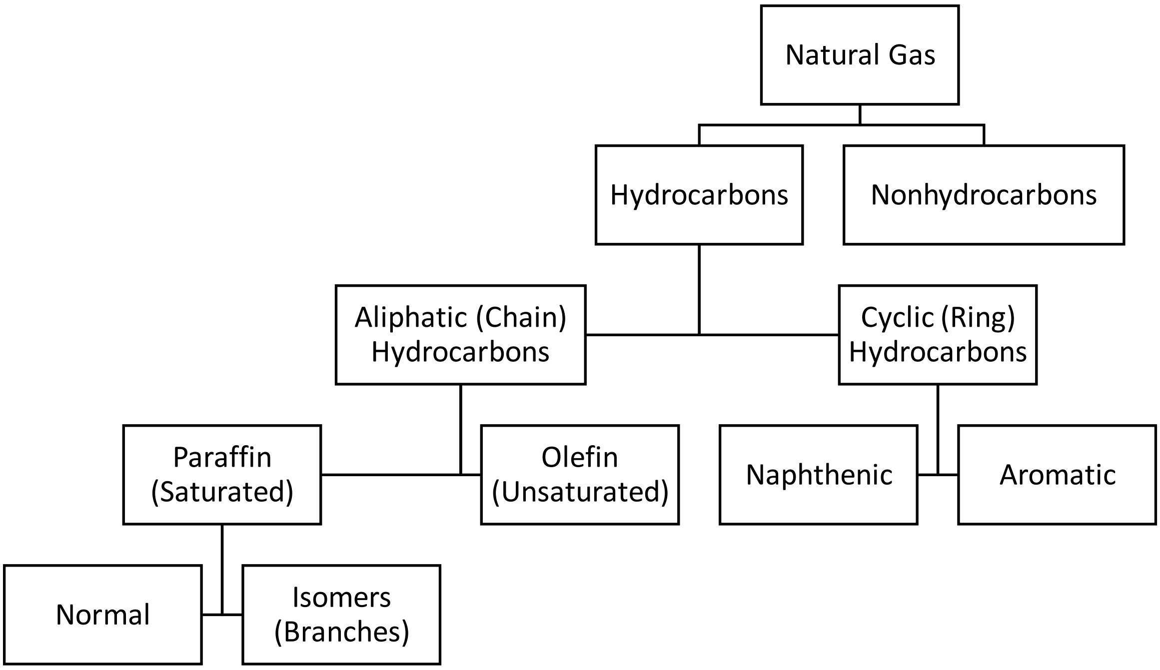
1. Definition of Natural Gas

Natural gas is defined as gas obtained from a natural underground reservoir. It generally contains a large quantity of methane along with heavier hydrocarbons such as ethane, propane, normal butane, isobutane, etc. Also, in the raw state it often contains a considerable amount of non-hydrocarbons, such as nitrogen, hydrogen suiphide and carbon dioxide. There are some traces of such compounds as helium, carbonyl sulphide and various mercaptan. It is also generally saturated with water. Table 1. below give some examples of the analysis of various types of gas.

Table 1: Typical Raw Gas Composition

Component	Typical Analysis (mole %)
Methane	> 85
Ethane	3 – 8
Propane	1 - 2
n-Butane	> 0.48
Isobutane	> 0.25
n-Pentane	> 0.21
Isopentane	> 0.15
Hexane	> 0.47
Heptane plus	-
N_2	1 – 5
H_2S	< 1
CO_2	1 – 2

2. Chemical Composition of Natural Gas



2.1 Hydrocarbons

2.1.1 Aliphatic or Chain Hydrocarbons

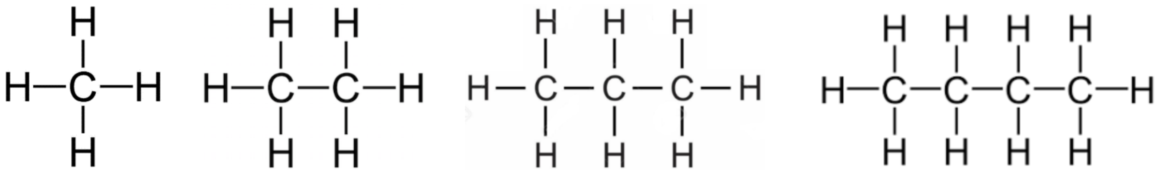
Aliphatic hydrocarbons occur in two forms: **paraffin** hydrocarbons and **olefin** hydrocarbons. The most common are **saturated hydrocarbons**.

- CH_4 - Methane (predominant)
- C_2H_6 - Ethane
- C_3H_8 - Propane
- C_4H_{10} – Butane
- C_5H_{12} – Pentane
- C_6H_{14} – Hexane

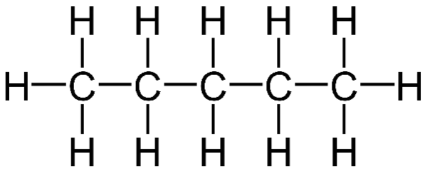
Paraffin

Paraffin includes **normal and isomers saturated hydrocarbons**.

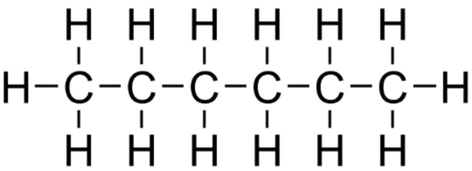
Normal paraffin



Methane *Ethane* *Propane* *Normal Butane*



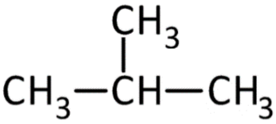
Normal Pentane



Normal Hexane

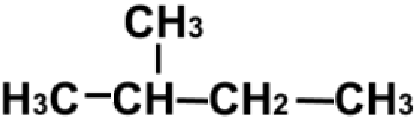
Isomers

Isomers are compounds having the same composition and molecular weight but different properties due to a different structural arrangement. The structural formulae for butane isomers are as follows:



$CH_3-CH(CH_3)-CH_3$

Isobutane



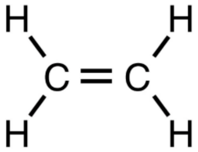
$H_3C-CH(CH_3)-CH_2-CH_3$

Isopentane

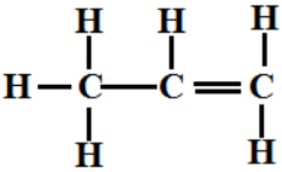
Olefin hydrocarbons

Olefin hydrocarbons have the general formula of C_nH_{2n} and are classed as **unsaturated hydrocarbons**. They usually occur only in traces.

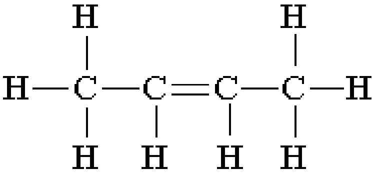
- C_2H_4 – Ethene.
- C_3H_6 – Propene.
- C_4H_8 – Butene.



Ethene



Propene



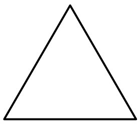
Butene

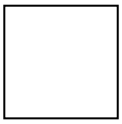
2.1.2. Cyclic or Ring Hydrocarbons

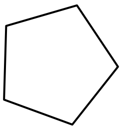
Cyclic hydrocarbons also occur in traces most of the time. They are two kinds: **naphthenic**, and **aromatic** hydrocarbons.

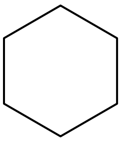
Naphthenic hydrocarbons

Naphthenic hydrocarbons are **saturated cyclic hydrocarbons** with the general formula of C_nH_{2n}


Cyclopropane

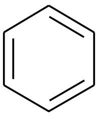

Cyclobutane

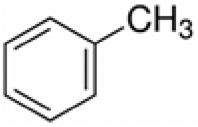

Cyclopentane


Cyclohexane

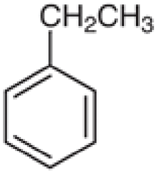
Aromatic hydrocarbons

Aromatic hydrocarbons are **unsaturated cyclic hydrocarbons** classified by the number of six—carbon rings in the molecule. The structures of benzene, toluene, and ethyl benzene are as follows:


Benzene

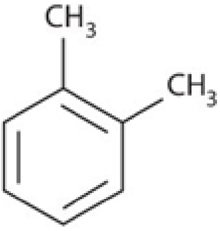


Toluene (Methyl benzene)

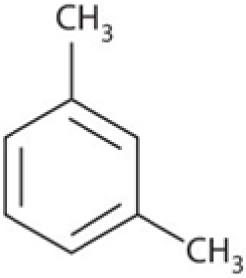


Ethyl benzene

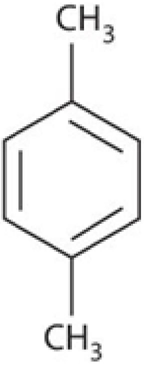
Structures of more complex aromatics such as **xylenes** in which two or more methyl groups or side chains are attached to the benzene ring are shown below:



Orthoxylene



Metaxylene



Paraxylene

2.2 Nonhydrocarbon Components

Some non-hydrocarbon components of natural gas are as follows:

Nitrogen	N_2
Carbon dioxide	CO_2

Hydrogen sulfide	**H_2S**
Helium	**He**
Water vapor	**H_20**
Carbonyl sulfide	**COS**
Carbon disulfide	**CS_2**
Sulfur	**S**
Mercaptans	**RSH**

Note: R represents an alkyl group

Methyl Mercaptan and Ethyl Mercaptan

Methyl mercaptan and **ethyl mercaptan** are the two mercaptan compounds most commonly found in natural gas. Their structures are as follows:

- CH_3SH (methyl mercaptan) Methanethiol
- CH_3CH_2SH (ethyl mercaptan) Ethanethiol

Mercaptans are the organic components of hydrocarbons with sulfur; they also have a bad smell and corrosive properties in pipeline transmission. It is the additive that is added to natural gas to make it easier to detect in case of a leak. If mercaptans are in high concentration in natural gas, these must be removed to reduce the value to an acceptable limit.

2.3 Classification of Natural Gas

There are two different classifications of natural gas:

First classification: This classification divides natural gas into two types:

1) **Hydrocarbon gases** (methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}) and hexane (C_6H_{14})).

2) **Non-hydrocarbon gases** (hydrogen (H_2), nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S) and inert gases (helium (He), argon (Ar), krypton (Kr) and radon (Rn)).

Table 2: Hydrocarbon gases

Name	Symbol	Molecular formula
Methane	C_1	CH_4
Ethane	C_2	C_2H_6
Propane	C_3	C_3H_8
Butane	C_4	C_4H_{10}
Pentane	C_5	C_5H_{12}
Hexane	C_6	C_6H_{14}

Second classification: This classification depends on the origin and therefore the natural gases are divided into three types (Fig. 1).

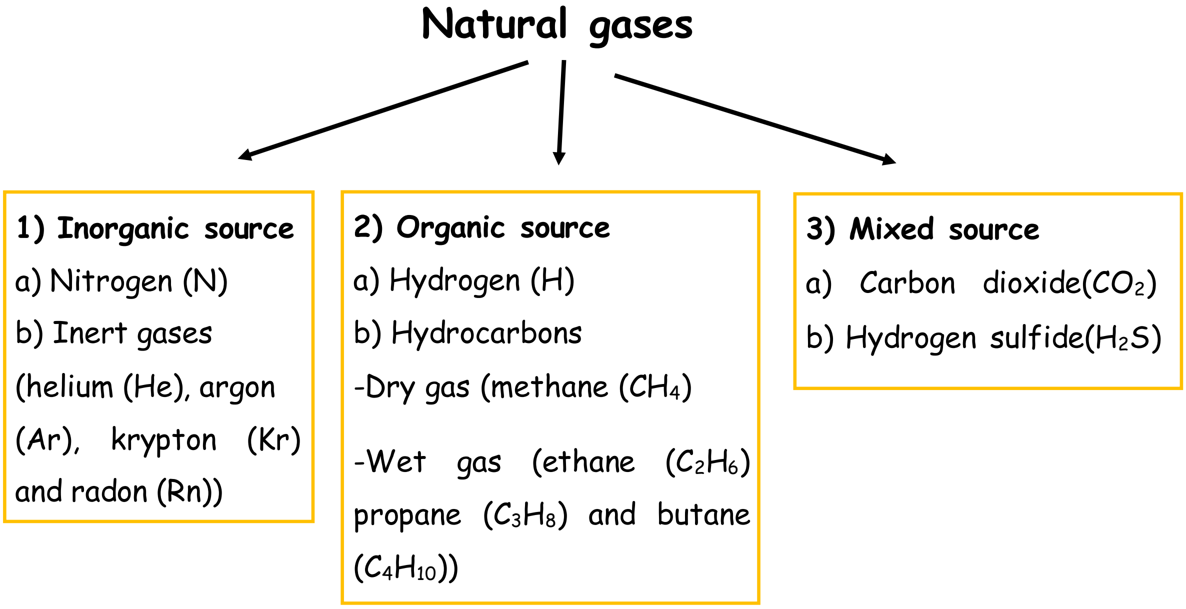


Figure 1. Classification of natural gas.

2.4 Classification of Hydrocarbon Gases

Based on the methane content, there are two general types of hydrocarbon gases:

Biogenic gas (≥95% methane), **or dry gas,** which was formed by bacterial decay at shallow depth.

Thermogenic gas (<95% methane), **or wet gas,** which is a lower quality gas formed at high temperatures. Wet gas on the other hand contains compounds such as ethane and butane, in addition to methane.

2.5 Natural Gas Utilization

Natural gas provided about 23% of the total world energy supply. Natural gas uses include transportation, commercial and electric generation. The industrial sector uses natural gas as a fuel for process heating, in combined heat and power systems, and as a raw material (feedstock) to produce chemicals, fertilizer, and hydrogen sources.

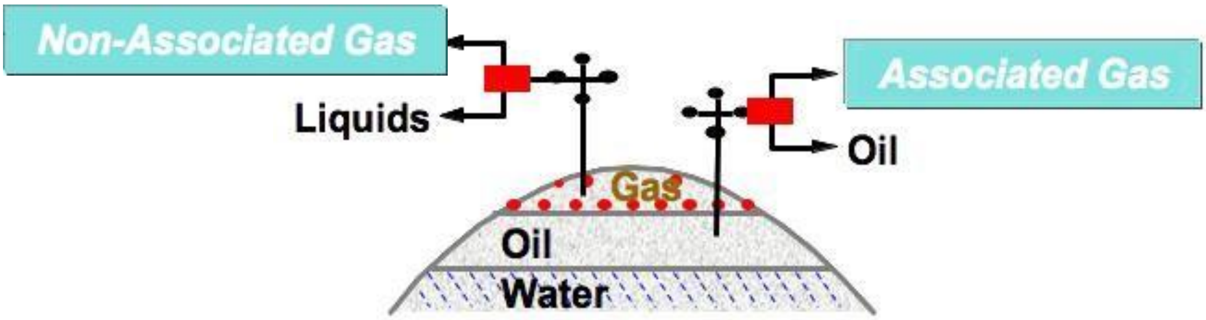
2.6 Types of Gas Reservoirs

There are three types of gas reservoirs:

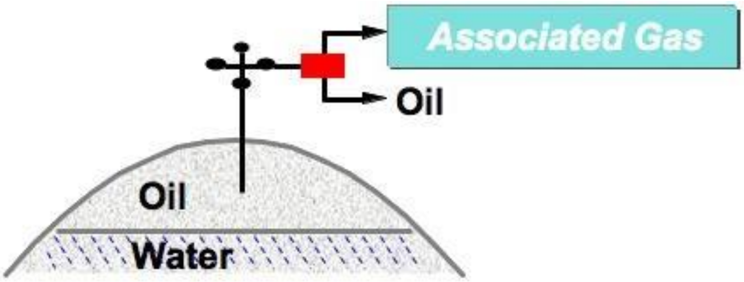
1) **Dry gas reservoir**: All mixture stays in vapor state.
2) **Wet gas reservoir**: All mixture stays in vapor state with a small amount of liquid.
3) **Gas condensate reservoir**: It is also called natural gas liquids. It is a low-density mixture of hydrocarbon liquids that are present as gaseous components in the raw natural gas.

2.7 Associated and Non-Associated Gases

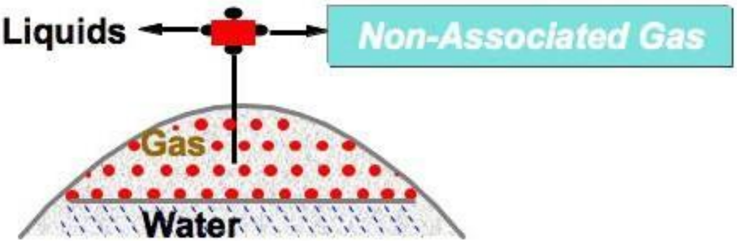
1) **Associated gases**: They are gases produced as a byproduct of the production of crude oil.
2) **Non-associated gas**: They are gases produced as a primary production of natural gas.



Condensate well



Crude oil well



Gas well

Figure 2. Associated and non-associated gases.

2.8 NATURAL GAS PROPERTIES

Natural gas is colorless, odorless, tasteless, shapeless, and lighter than air (see Table 3). The natural gas after appropriate treatment for acid gas reduction and after moisture and hydrocarbon dew point adjustment would then be sold within prescribed limits of pressure, heating value, and possibly Wobbe Index (often referred to as the Wobbe Number). One of the principal uses of natural gas is as a fuel, and consequently, pipeline gas is normally bought and sold on the basis of its heating value that can be produced by burning the gas. The heating value of natural gas is variable and depends on its accumulations, which are influenced by the amount and types of gases they contain.

Table 3 Properties of Natural Gas

Properties	Value
Relative molar mass	17–20
Carbon content, weight	% 73.3
Hydrogen content, weight	% 23.9
Oxygen content, weight	% 0.4
Hydrogen/carbon atomic ratio	3.0–4.0
Relative density, g/cm^3	15 ^oC 0.72–0.81
Boiling point,	^oC –162
Autoignition temperature	^oC 540–560
Octane number	120–130
Methane number	69–99
Stoichiometric air/fuel ratio, weight	17.2
Vapor flammability limits, volume	% 5–15
Flammability limits	0.7–2.1
Lower heating/calorific value, MJ/kg	38–50
Stoichiometric lower heating value,	MJ/kg 2.75
Methane concentration, volume	% 80–99
Ethane concentration, volume	% 2.7–4.6
Nitrogen concentration, volume	% 0.1–15

2.9 IMPURITIES

Natural gases contain impurities in varying amounts. This constitutes serious problems. Therefore, gas treatment required to reduce the impurities to minimum level.

Types of Impurities

1) Carbon dioxide (CO_2).
2) Oxygen (O_2).
3) Nitrogen (N_2).
4) Hydrogen sulfide (H_2S).
5) Sulfur compounds.
6) Water (H_2O).
7) Helium (He).
8) Mercury (Hg).
9) Dust.

Effect of Hydrogen sulfide (H_2S)

1) The hydrogen sulfide is present in all gas reservoirs.
2) The presence of H_2S will combine with water to produce corrosive acids.

$$H_2S + 4H_2O \rightarrow H_2SO_4 + 4H_2$$

3) The flare of natural gas containing H_2S will result in sulfur dioxide (SO_2) which is very toxic (health and environment).

Effect of Carbon dioxide (CO_2)

1) The carbon dioxide is present in all gas reservoirs.
2) The main production problem is the corrosive acids performed in the presence of water.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

3) Another problem would be the lowering of the heat content of natural gas.

Effect of Water (H_2O)

1) Every gas reservoir has certain initial liquid water saturation.
2) The presence of H_2O will combine with CO_2 and/or H_2S to produce corrosive acids.
3) The presence of H_2O will reduce the area available for gas flow.
4) When the temperature of the natural gas falls below a certain limit allows the water and gas molecules and form a solid phase know as hydrates.

Hydrate Formation Conditions

1) Hydrates are ice-like solids that form when free water and natural gas combine at high

pressure and low temperature.

2) The structure of hydrates consists of several water molecules associated with each hydrocarbon molecules.
3) Duo to this reason the water should be removed from the natural gas and the gas stream must be dehydrated to certain minimum limits.

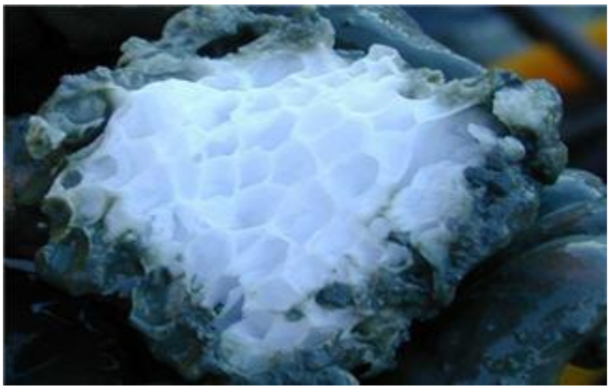


Figure 3. Natural gas hydrates.

2.10 WORLD PICTURE FOR NATURAL GAS

The current status of primary energy sources is summarized in Figure 4. Basically, natural gas, coal and crude oil represent the majority source of energy in the world.

Six countries possess two thirds of the world’s gas reserves (Figure 5), with almost half of the reserves located in Iran and Russia. The total reported natural gas reserves (~6,040 Trillion cubic feet [Tcf] at the beginning of 2005 [Energy Information Administration, 2005c]) do not include discovered reserves that are not economically feasible to bring to market. This “stranded gas” resides in remote regions, where the reserve size does not justify the cost of the infrastructure required to bring it to market. Note that proven reserve estimates are truly estimates and vary among sources.

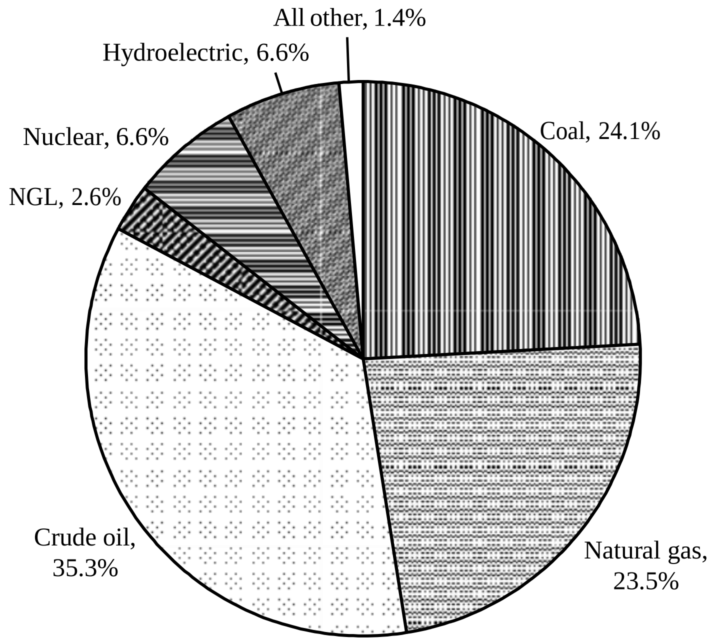


Figure 4. Primary sources of energy in the world in 2003. Total energy used was 405 quadrillion Btu (Energy Information Administration, 2005b).

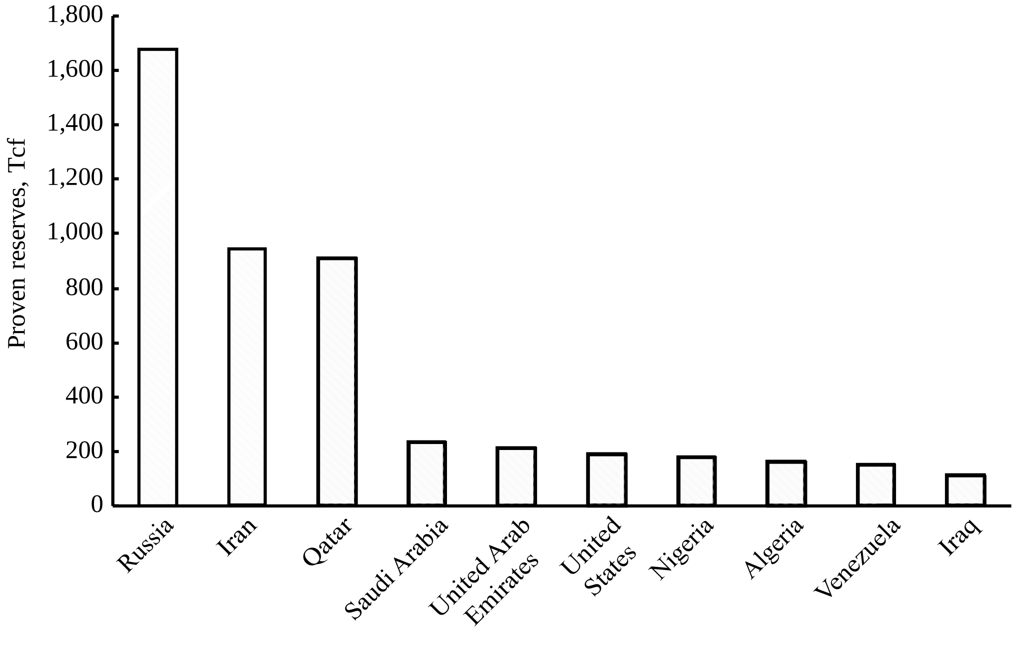


Figure 5. Major proven natural gas reserves by country. Total proven reserves estimated to be 6,040 Tcf (Energy Information Administration, 2005c).

2.11 Natural Gas Processing

Natural-gas processing is carried out to clean raw natural gas by separating impurities and various non-methane hydrocarbons and fluids to produce what is known as pipeline quality dry natural gas. Raw natural gas usually contains some impurities such as H_2S, CO_2, water vapor, and other sulfur compounds. Natural gas that contains more than 5.7 milligrams of H_2S per one cubic meter of natural gas (which is equivalent to approximately 4 ppm by volume) under standard temperature and pressure is called "sour natural gas". It is usually desirable to remove H_2S, CO_2 and H_2O to prevent corrosion problems in the first place and to increase the heating value of the natural gas by eliminating CO_2. In this regard, sweetening of natural gas is a vital step for three main reasons:

1. Health hazards: exposure to 500 ppm of H_2S in 0.5 to 1 hr could be caused breathing problems and death can be expected in minutes.
2. Sales contracts: the allowable limit is less than 3.5 ppmv H_2S in natural gas.
3. The main benefit obtained from the removal of both of these acid gases (H_2S and CO_2) from a pipeline stream is to minimize the corrosion effects. In addition, the recovery of sulfur represents a commercial incentive.

In general, natural gas processing includes the following steps:

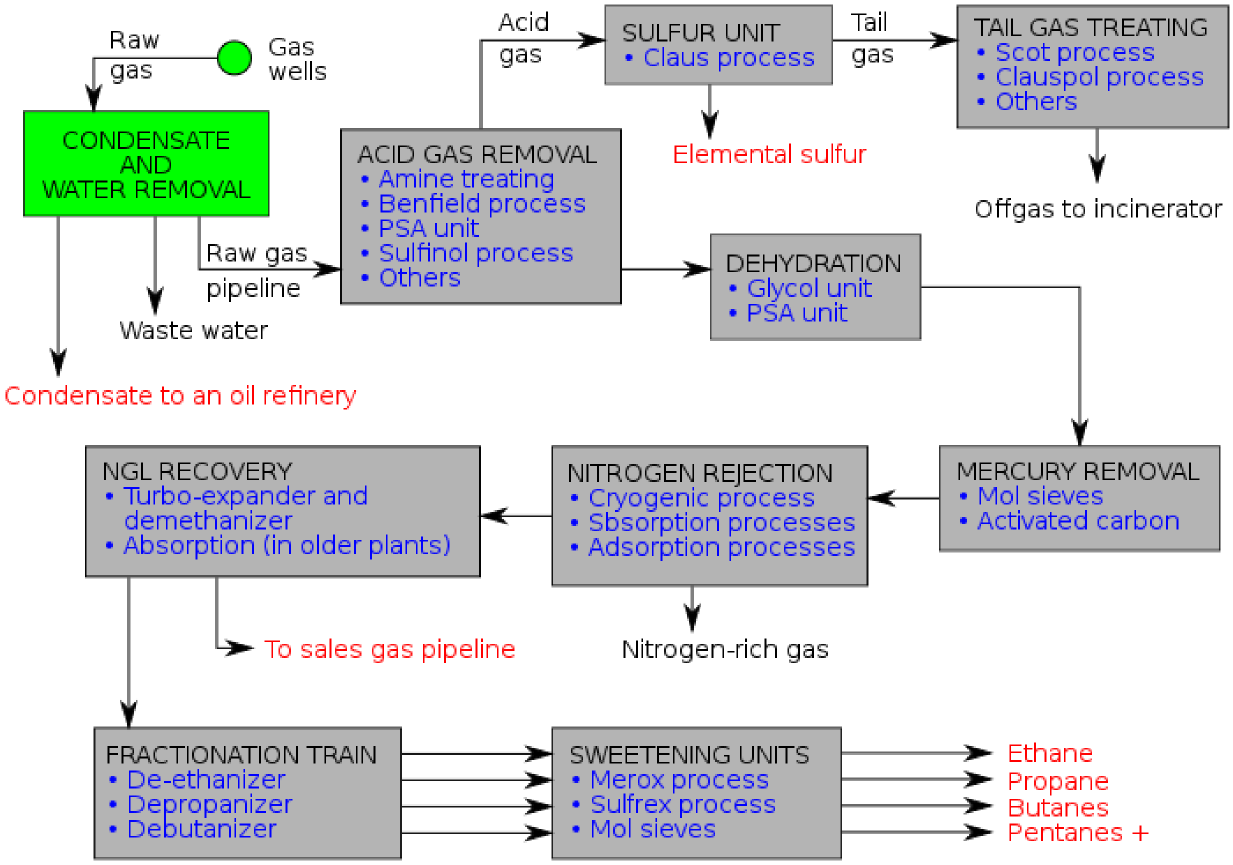
- Condensate and Water Removal
- Acid Gas Removal
- Dehydration (moisture removal)
- Mercury Removal
- Nitrogen Rejection
- NGL Recovery, Separation, Fractionation, and Treatment of Natural Gas Liquids

In addition to these processes, it is often necessary to install scrubbers and heaters at or near the wellhead. The scrubbers remove sand and other large-particle impurities. The heaters ensure that the temperature of the natural gas does not drop too low and form a hydrate with the water in the gas stream. Natural gas hydrates are crystalline ice-like solids or semi-solids that can impede the passage of natural gas through valves and pipes.

A generalized natural gas flow diagram is shown in Figure 6. After initial scrubbing to remove particles, the first step in natural gas processing is the removal of condensate (oil) and water that is achieved by controlling the temperature and pressure of the inlet stream from the well, as shown in Figure 6. Gas separated in this unit is sent to acid gas recovery; the condensate or the oil recovered is usually sent to a refinery for processing, while water is disposed, or treated as wastewater.

Acid gases (H_2S and CO_2) are separated usually by absorption in an amine solution. The recovered

H_2S is sent to a combined Claus-SCOT (Tail Gas Treating) unit to be converted to elemental sulfur. After removing the acid gases, the natural gas stream is sent to a dehydration unit to remove water typically by absorption in a glycol unit, followed by mercury removal (by adsorption on activated carbons or other sorbents), and nitrogen rejection either cryogenically, or by adsorption, or absorption depending on the nitrogen concentration. The last step in the processing sequence is the Natural Gas Liquids (NGL) extraction, fractionation, and treatment.



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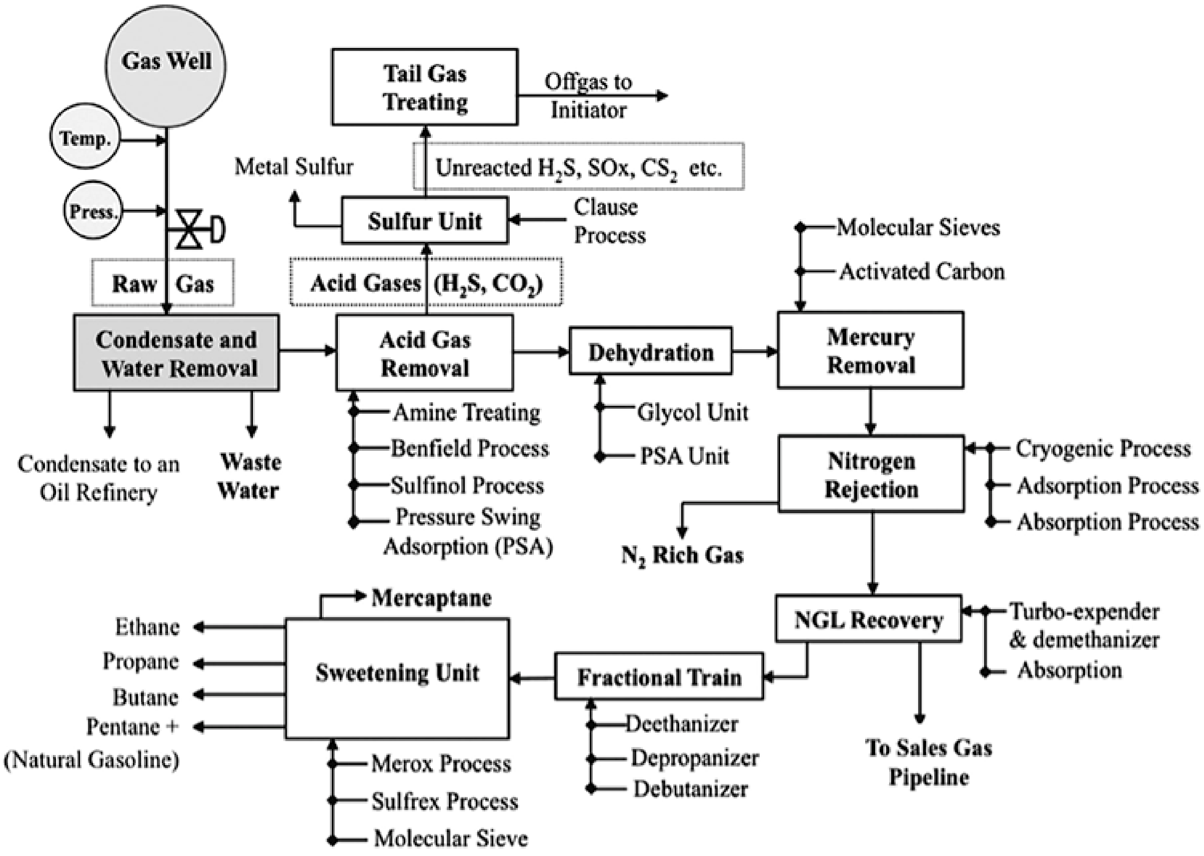


(B)

Figure 6. Schematic flow diagram of a typical natural gas processing plant.

2.11.1 Condensate and Water Removal

The raw natural gas feedstock from a gas well or a group of wells is cooled to reduce the gas temperature to below its hydrocarbon dew point at the feedstock pressure. This condenses a large part of the gas condensate hydrocarbons. The feedstock mixture of gas, liquid condensate and water is then sent to a high pressure separator vessel where the water and the raw natural gas are separated and removed. If a pressure boost is required, the raw natural gas from the high pressure separator is sent to the main gas compressor, which raises the pressure of the gases to whatever pressure is required for the pipeline transportation of the gas to the raw natural gas processing plant. The main gas compressor discharge pressure will depend upon the operating pressure of and the distance to the raw natural gas processing plant and may require a multi-stage compressor.

The gas condensate from the high pressure separator flows through a throttling control valve to a low pressure separator. The reduction in pressure across the control valve causes the condensate to undergo a partial vaporization referred to as flash vaporization. The raw natural gas from the low pressure separator is sent to a "booster" compressor that raises the gas pressure and sends it through a cooler, and then to the main gas compressor.

The water removed from both the high and low pressure separators may need to be processed to remove hydrogen sulfide (H_2S) before the water can be disposed of underground or reused in some fashion. The condensate is usually transported to a petroleum refinery.

Note:

The dew point of a gas is the temperature at which the water vapor or low-boiling hydrocarbon derivatives contained in the gas is transformed into the liquid state.

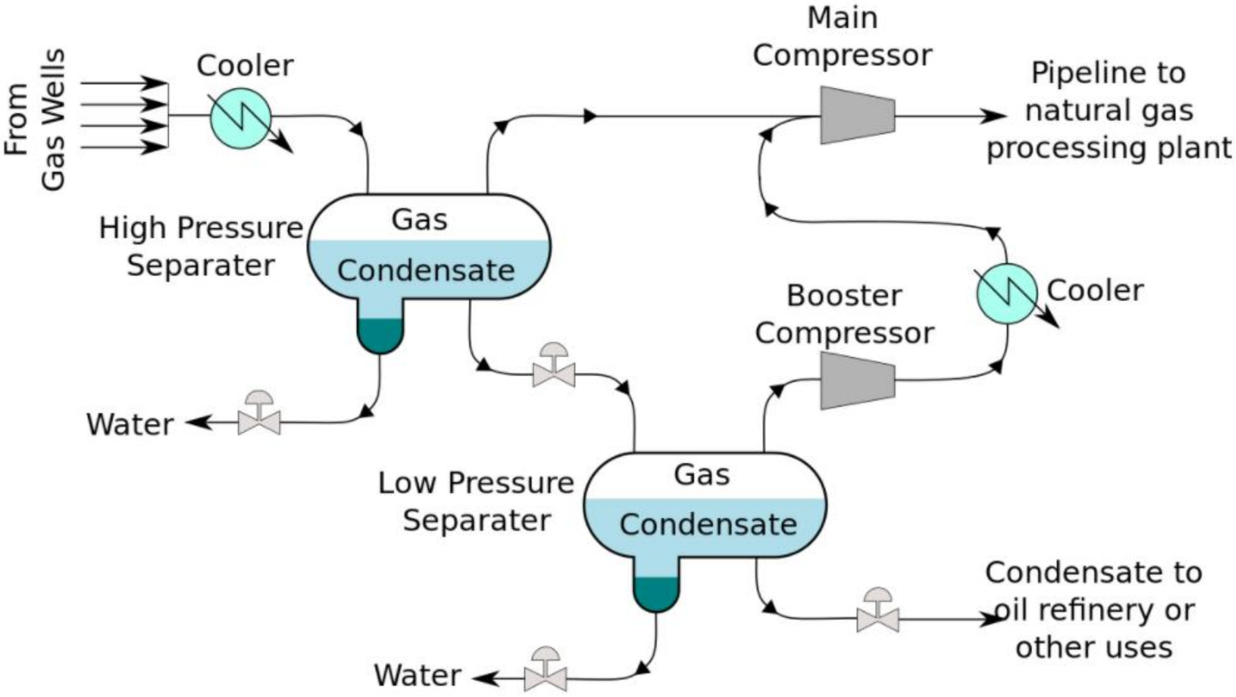


Figure 7. Schematic flow diagram of the separation of condensate from raw natural gas.

2.11.2 Acid Gas Removal (Sweetening of Sour Natural Gas)

The raw gas is then pipelined to a gas processing plant where the initial purification is usually the removal of acid gases (hydrogen sulfide and carbon dioxide). There a many processes that are available for that purpose as shown in the flow diagram, but amine gas treating is the most widely used process. In the last ten years, a new process based on the use of polymeric membranes to dehydrate and separate the carbon dioxide and hydrogen sulfide from the natural gas stream is gaining acceptance.

These processes use an aqueous solution of a weak base in order to react chemically along with absorption of the acid gases (H_2S or CO_2) to be removed from the natural gas. Absorption is attributed to the rate of mass transfer driven by the difference in partial pressure between the bulk of gas and the liquid. Reactions are identified as chemical-absorption, or chemi-sorption. They are reversed by the effect of temperature or pressure, which results in regeneration of the solvent used. The common treating solutions are aqueous solutions of the ethanol amines: mono ethanol amine (MEA), di-ethanol amine (DEA), tri-ethanol amine (TEA), or di-glycol amines (DGA). The amine sweetening process is schematically outlined in Figure 8. It consists basically of contactor and a regenerator, where reaction occurs at 100 °F, while regeneration takes place at 240 °F:

$$H_2S + HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 \underset{240\,F}{\overset{100\,F}{\rightleftarrows}} HO\text{-}CH_2\text{-}CH_2\text{-}NH_3.HS$$

Reaction could be applied to CO_2 as well. The ethanol-amine processes are recommended when the partial pressure of the acid gas is low/and or low levels of acid gas are desired in the residue gas. If the quantity of acid gas is large, hot potassium carbonate followed by amine treatment may be justified.

The absorber involves a mass transfer operation (gas/liquid) in which the sour gas flows into the bottom of the column (contactor) and moves upward countercurrent to the solvent (which is amine-solution).

Regenerator it involves a mass transfer operation (stripping), where the rich amine flows into the regenerator stripping column, near the top, flows downward by gravity contacting the hot gases from the re-boiler. Acid gases are removed from solution, while lean amine is cooled first, then re-circulated back to the absorber.

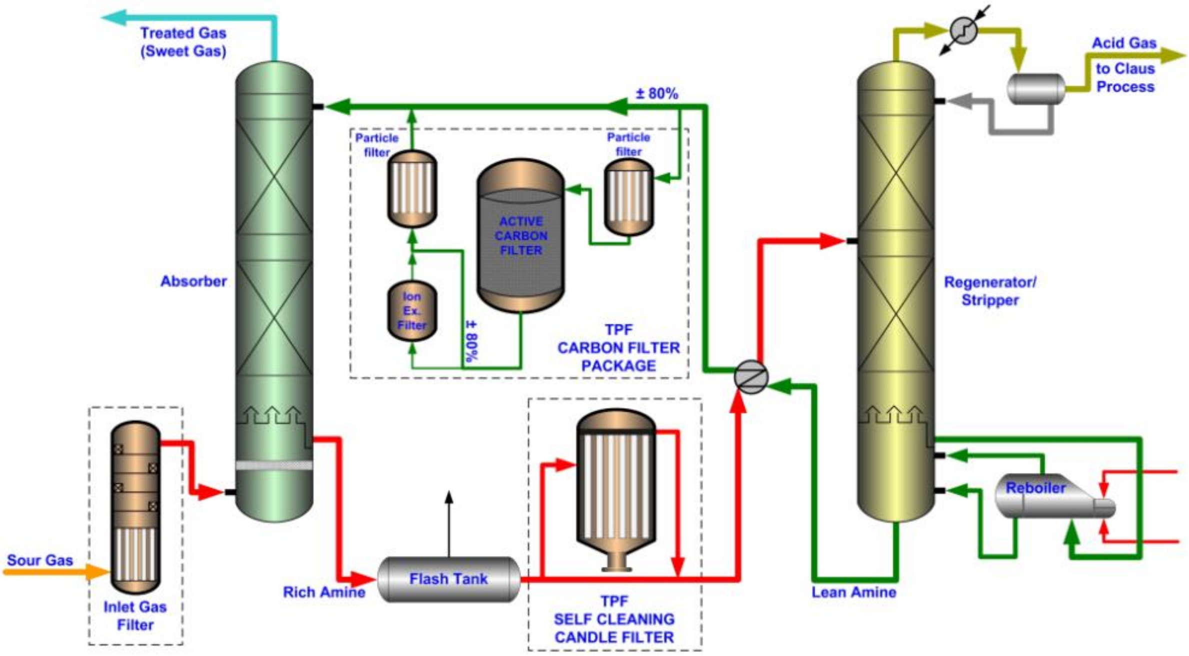


Figure 8. A typical amine gas sweetening plant.

2.11.3 Sulfur recovery unit (Claus process)

The acid gases removed by amine treating are then routed into a sulfur recovery unit which converts the hydrogen sulfide in the acid gas into elemental sulfur. There are a number of processes available for that conversion, but the Claus process is by far the one usually selected. The residual gas from the Claus process is commonly called tail gas and that gas is then processed in a tail gas treating unit (TGTU) to recover and recycle residual sulfur-containing compounds back into the Claus unit. The final residual gas from the TGTU contains N_2, CO_2, CO, H_2O, H_2, unreacted H_2S, COS, CS, sulfure vapor etc. All these gases are incinerated and passed to atmosphere. Thus, the carbon dioxide CO_2 in the raw natural gas ends up in the incinerator flue gas stack.

Claus process description

The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes. The by-product gases mainly originate from physical and chemical gas treatment units in refineries, natural gas processing plants and gasification or synthesis gas plants. Gases with an H_2S content of over 25% are suitable for the recovery of sulfur in straight-through Claus plants while alternate configurations such as a split-flow set up or feed and air preheating can be used to process leaner feeds.

Hydrogen sulfide produced in the acid gas removal unit is converted to sulfur in Claus plant. The reaction proceeds in two steps:

$$2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$$
$$4\ H_2S + 2\ SO_2 \rightarrow 3\ S_2 + 4\ H_2O$$

The Claus technology can be divided into two process steps, thermal and catalytic step. The Sulfur Recovery Unit is based on the modified Claus Process, which is a two-step reaction scheme overall. A portion of the total H_2S is burned in the Reaction Furnace to form SO_2. Then, the H_2S and SO_2 react, at an optimal 2:1 ratio, to form elemental Sulfur across the Claus Catalytic Reactors. After each catalytic stage, liquid sulfur is recovered in the Claus Condensers. The remaining unreacted H_2S and SO_2 then proceed to the next stage, where the equilibrium-limited Claus reaction continues in the presence of Claus catalyst. The overall effecinciy of the claus process to recover the sulfur about 96-97%.

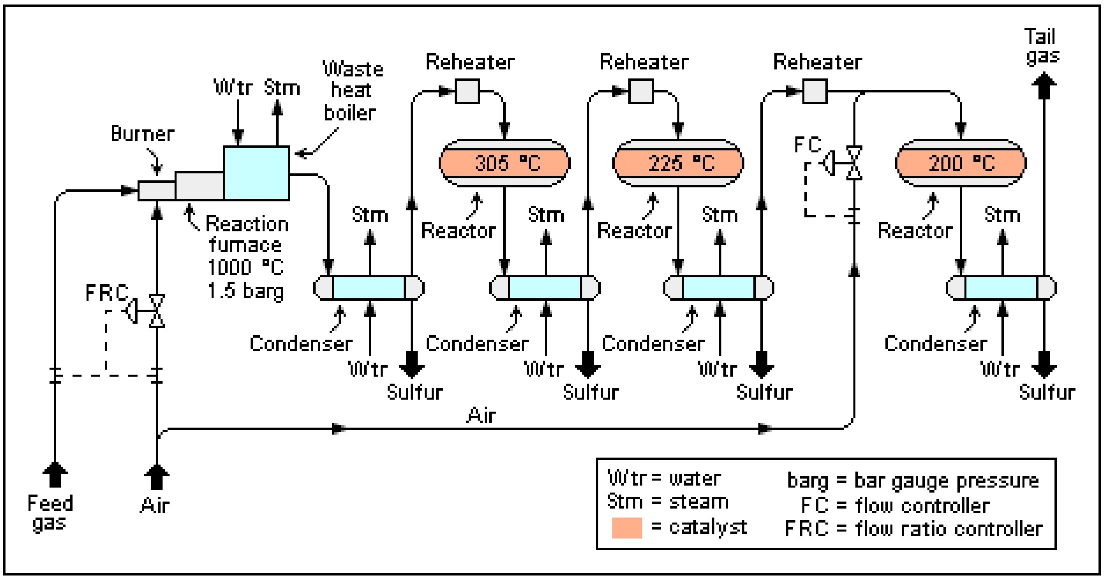


Figure 9. Schematic flow diagram of a straight-through, 3 reactor (converter), Claus sulfur recovery unit.

2.11.4 Dehydration (moisture removal)

Dehydration process is a process used to remove the water from natural gas. It is the most common and economical means of water removal from natural gas. Glycols typically seen in industry include triethylene glycol (TEG), diethylene glycol (DEG), ethylene glycol (MEG), and tetraethylene glycol (TREG). TEG is the most commonly used glycol in industry.

Dehydration process description

In this process, lean glycol (purity >99%) is fed to the top of an absorber tower (also known as a "glycol contactor") where it is contacted with the wet natural gas stream. The glycol removes water from the natural gas by physical absorption and is carried out the bottom of the column. Upon exiting the absorber the glycol stream is often referred to as "rich glycol". The dry natural gas leaves the top of the absorption column and is fed either to a pipeline system or to a gas plant. Glycol absorbers can be either tray columns or packed columns.

After leaving the absorber, the rich glycol is fed to a flash vessel where hydrocarbon vapors are removed and any liquid hydrocarbons are skimmed from the glycol. This step is necessary as the absorber is typically operated at high pressure and the pressure must be reduced before the regeneration step. Due to the composition of the rich glycol, a vapor phase having a high hydrocarbon content will form when the pressure is lowered.

After leaving the flash vessel, the rich glycol is heated in a cross-exchanger and fed to the stripper (also known as a regenerator). The glycol stripper consists of a column, an overhead condenser, and a reboiler. The glycol is thermally regenerated to remove excess water and regain the high glycol purity. The hot, lean glycol is cooled by cross-exchange with rich glycol entering the stripper. It is then fed to a lean pump where its pressure is elevated to that of the glycol absorber. The lean solvent is cooled again with a trim cooler before being fed back into the absorber. This trim cooler can either be a cross-exchanger with the dry gas leaving the absorber or an air-cooled exchanger.

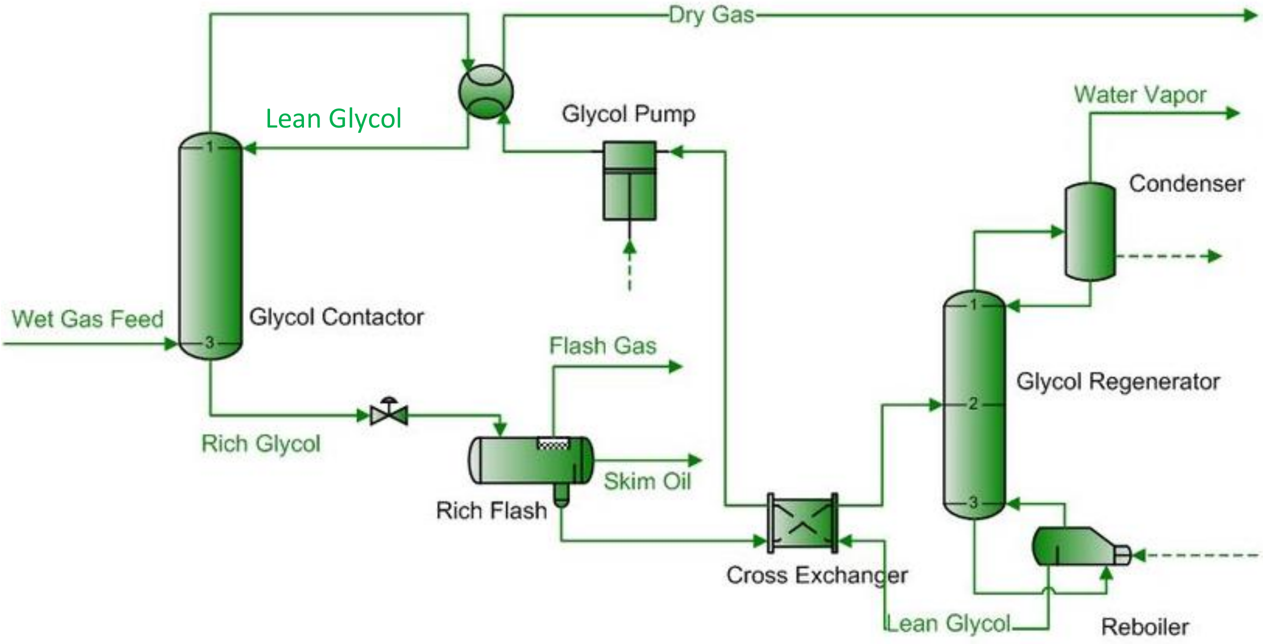


Figure 10. Process flow diagram for natural gas dehydration using glycol.

2.11.5 Mercury removal from natural gas

Two major problems are associated with the presence of mercury in natural gas: amalgam formation with aluminium and environmental pollution. Mercury corrodes brazed-aluminum heat exchangers as it amalgamates with the aluminum to weaken the material. Elemental mercury is toxic to humans as well as a poison to many catalysts. Mercury may be present in elemental form or as organometallic compounds, such as dimethylmercury, methylethylmercury, and diethylmercury, or as inorganic compounds such as $HgCl_2$. The allowable concentrations of mercury should be reduced to certain values less than 0.01 $\mu g/Nm^3$ before the gas transfer to another process.

Mercury removal process description

Mercury can be removed using either non-regenerative or regenerative adsorbents. In both cases hydrocarbon gas enters the top of an adsorption tower and flows downward through the adsorbent where the mercury is adsorbed, exiting the bottom for further processing or sale. Regenerable systems have two or more adsorption towers enabling one to be regenerated while the remaining tower(s) are in operation. Bed regeneration is accomplished by flowing heated regeneration gas upward so that contaminants adsorbed near the inlet can be removed without flushing them through the entire bed. Protection of the beds from liquid water contamination is critical to ensure effective mercury removal and long, reliable bed life.

Nonregenerative process

The nonregenerative processes use sulfur impregnated on a support such as activated charcoal or alumina to provide a large surface area. In this process, the mercury reacts with the sulfur to form a stable compound on the adsorbent surface.

Regenerative process

The regenerative process utilizes silver on molecular sieve to chemisorb elemental mercury while providing dehydration at the same time. The silver-impregnated sieve is added to the standard molecular sieve dehydration bed, and the basic dehydration process remains unchanged. Essentially, all of the mercury condenses with the water on regeneration and forms a separate phase, which easily can be decanted and sold.

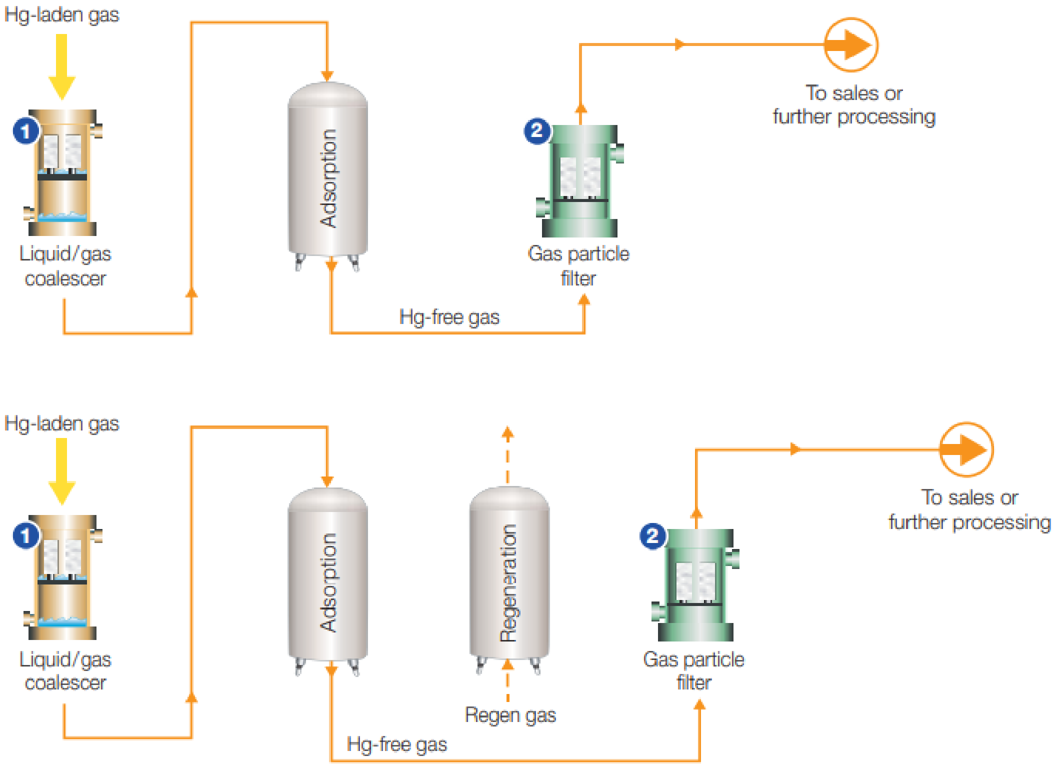


Figure 11. Process flow diagram for mercury removal from natural gas.

2.11.6 Nitrogen rejection

Raw natural gas contains the inert gas nitrogen. Nitrogen lowers the heating value of natural gas and increases transport volumes. Therefore, removing nitrogen assessts to increase the thermal efficiency of the natural gas. Three basic methods are used for removal of nitrogen from natural gas:

- Cryogenic process
- Adsorption process
- Absorption process

Cryogenic process

A nitrogen rejection unit (NRU) selectively removes nitrogen from a gas. The name can be applied to any system that removes nitrogen from natural gas. For high flow-rate applications, typically above 420 thousand cubic metres per day at standard pressure, cryogenic processing is the norm. This is a distillation process which utilizes the different volatilities of methane (boiling point of -258.9 °F) and nitrogen (boiling point of -320.4°F) to achieve separation. In this process, a system of compression and distillation columns drastically reduces the temperature of the gas mixture to a point where methane is liquefied and the nitrogen is not. For smaller applications, a series of heat exchangers may be used as an alternative to distillation columns.

Cryogenic process description

The most common method of removing nitrogen from natural gas is cryogenic distillation. The feed concentrations usually below 20% N_2, a single-column design can be used. For higher concentrations, a dual-column is better. With the addition of a recycle compressor, it can be used at lower N_2 contents. Figure 12 shows a flow diagram for a two-column NRU receiving feed that contains 15% N_2 from the mercury removal unit. Gas from the mercury removal unit is cooled by heat exchange and pressure reduction and fed to a distillation column operating at 200 psig (14 barg). The bottoms product from this high-pressure column is reduced in pressure to cool the stream to −240°F (−151°C). This stream, combined with the bottoms product from the second low-pressure column, is fed to a heat exchanger in the top of the high-pressure column to provide the necessary reflux. The overhead from the high-pressure column flows through three heat exchangers, is reduced in pressure to approximately 15 psig (1 barg), and enters the low pressure column at −300°F (−184°C). The overhead from this column is 98% N_2, and the bottoms product is approximately 98% N_2-free gas.

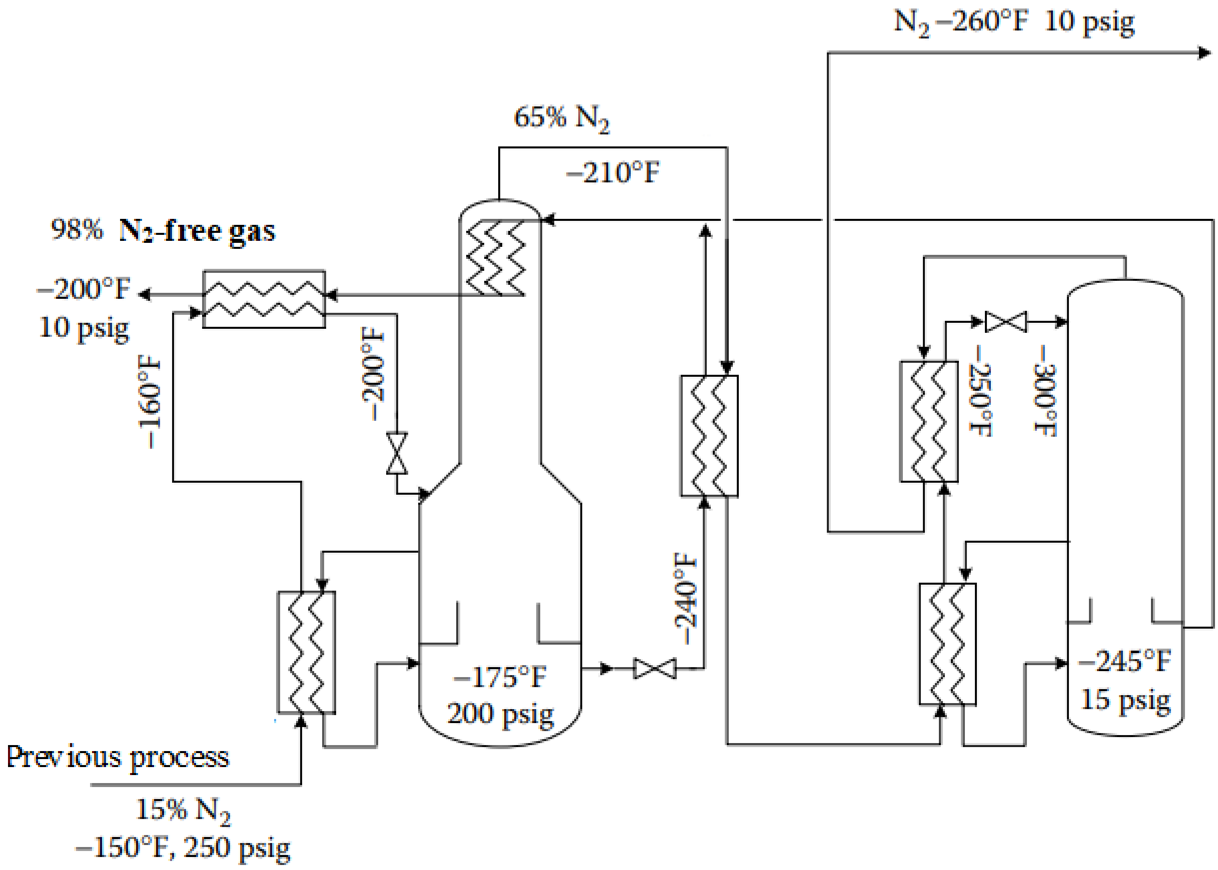


Figure 12. Nitrogen Recovery Unit (NRU) by use of two-column cryogenic distillation.

2.11.7 NGL Recovery

The natural gas is processed in this unit to remove the heavier hydrocarbon liquids from the natural gas stream. These heavier hydrocarbon liquids, commonly referred to as natural gas liquids (NGL), include ethane, propane, butanes, and natural gasoline (pentane+). Recovery of NGL components in gas may be required for hydrocarbon dew point control in a natural gas stream (to avoid the unsafe formation of a liquid phase during transport) and to obtain a good source of revenue, as NGLs normally have significantly greater value as separate marketable products than as part of the natural gas stream. Lighter NGL fractions, such as ethane, propane, and butanes, can be sold as fuel or feedstock to refineries and petrochemical plants, while the heavier portion (pentane+) can be used as gasoline-blending stock. NGL can be recovered using one of two processes: Cryogenic turbo-expender and demethanizer process or absorption process.

Cryogenic turbo-expender process

The base diagram of a turboexpander process for a rich natural gas is shown in Fig. 1. Cryogenic processing consists of lowering the temperature of the gas stream to around –95°C. In this process, external refrigerants are used to cool the natural gas stream. The expansion turbine is used to rapidly expand the chilled gases, causing the temperature to drop significantly.

Cryogenic turbo-expender process description

The raw gas at high pressure (often 70 barg) is first cooled against the demethanizer overhead stream, and is then cooled to approximately – 40°C in the evaporator of a propane closed-loop refrigeration package. The resulting two-phase flow is separated in the first separator; the liquid is sent to the demethanizer, and the gas (after further cooling and separation) is expanded, generally to 30 barg, in a turboexpander, where its enthalpy variation turns into mechanical work. The cold two-phase stream from the expander heads to the demethanizer, where the light components dissolved in the condensate are stripped out according to the operating mode. The NGL are extracted from the bottom of the demethanizer and routed to the fractionation section of the facility, while the residue gas (Natural Gas) is compressed in the compression end of the turboexpander.

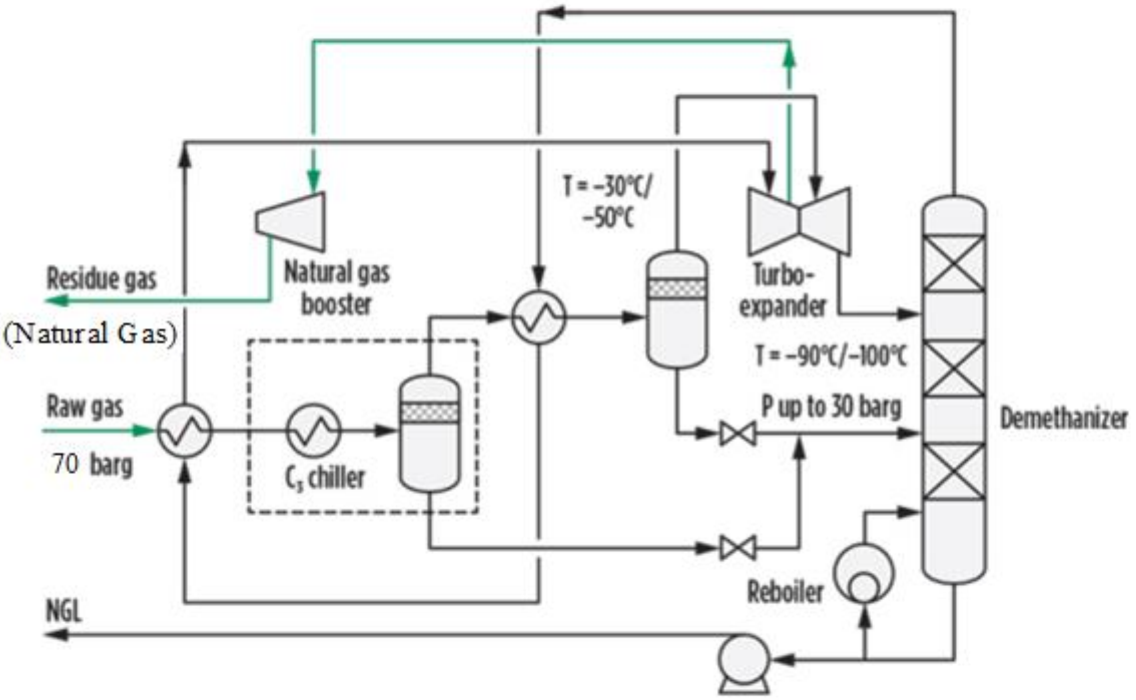
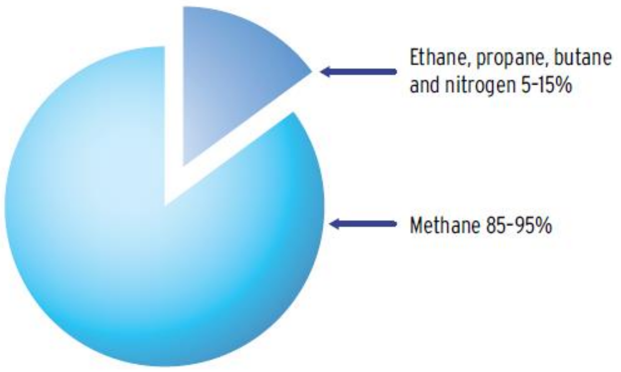
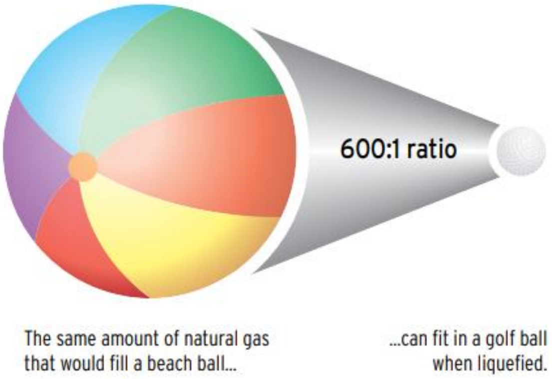


Figure 13. Cryogenic turbo-expander process flow diagram.

2.11.8 Liquefied Natural Gas (LNG)

Liquefied natural gas (LNG) technology has been proven to be effective over the past thirty years. When natural gas is cooled to approximately (–162 °C) at atmospheric pressure, a condensed liquid called liquefied natural gas forms. The volume reduction is about 1/600 the volume of natural gas at the burner tip. The physical properties of LNG allow for its long-distance transport by ship across oceans to markets and for its local distribution by truck onshore. Occasionally, liquefaction of natural gas also provides the opportunity to store the fuel for use during high consumption periods close to demand centers, as well as in areas where geologic conditions are not suitable for developing underground storage facilities. LNG is mostly methane plus a small percent of ethane, propane and butane, and trace amounts of nitrogen.





The same amount of natural gas that would fill a beach ball...

...can fit in a golf ball when liquefied.

Vedio of LNG (What is LNG? Turning natural gas into liquid | Natural Gas)

https://www.youtube.com/watch?v=QgtSoEJD9HE&t=168s&ab_channel=Shell

2.11.9 Compressed Natural Gas (CNG)

Natural gas can be transported in containers at high pressures. Compressed natural gas (CNG) refers to natural gas compressed to about 200 to 250 bar. Thanks to its high energy density and low emission values, it is a good fuel for powering vehicles, provided they are equipped with a suitable high-pressure tank. Using CNG as fuel reduces carbon monoxide and nitrogen oxide emissions by up to 80%, CO2 emissions by up to 25%, and the proportion of methane hydrocarbons by up to 73%. Another advantage of CNG is that its processing into a fuel doesn’t require any additives or complicated refining processes.

2.11.10 Natural Gas Liquids (NGL) Fractionation

Natural Gas Liquids (NGLs) fractionation is the process used in gas processing plants to separate hydrocarbon mixtures from natural gas into individual products. These NGLs are ethane, propane, butane, and pentanes as well as natural gasoline found in natural gas. Separation into components is carried out by relative volatility. The ease of separation is dependent on the relative volatility of the components within the products and the required purity of the product streams. The size and cost of the fractionation column are determined by the degree of separation required and the component volatility. Products with higher purity will require more trays, more reflux and larger diameter of the column and/or reduced product. A fractionation train is made up of a number of fractionators. The number of separators required depends on the number of components to be produced from the feed. Fractionation is considered an important method of producing products that can be used in the industry for different applications. Pure NGL products are used as feedstock by the petrochemical industry, in the production of motor gasoline by refineries and as fuel (ex. LPG) by industrial and residential consumers. A conventional process for fractionating the NGLs is shown in Figure 14. As can be seen, natural gas liquids are normally fractionated by boiling off the various fractions in sequence from the lighter to the heavier hydrocarbons. The process starts with the deethanizer, which separates ethane from the NGL stream. Next, the depropanizer separates the propane; then the debutanizer boils off the butane, leaving natural gasoline. In some units, a butane splitter (or deisobutanizer) then further separates normal butane and isobutane. The isobutane goes overhead, and the normal butane is drawn from the bottom of the tower.

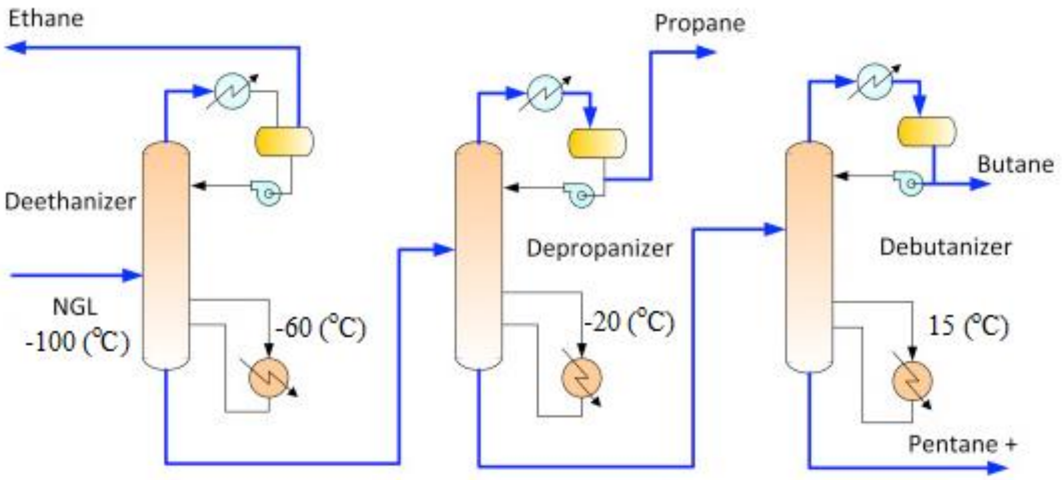


Figure 14. Typical fractionation process scheme.

Name	Molecular Formula	Boiling point(°C)
methane	CH_4	-161
ethane	C_2H_6	-89
propane	C_3H_8	-42
butane	C_4H_{10}	-1
pentane	C_5H_{12}	36
hexane	C_6H_{14}	69

2.12 Heating Value (HV) of Fuel

The enthalpy of a reaction (KJ/Kmole) refers to the difference between the enthalpy of products (H_{pro}) and reactants (H_{reac}) at a specified temperature and standard pressure of 1 atm for that reaction. The definition of the enthalpy of reaction:

$$\Delta H_R = H_{prod} - H_{reac}.$$

If a reaction involves either oxidation or combustion, then the enthalpy of reaction ΔH_R is termed as the enthalpy of combustion ΔH_C.

In fact, (**$\Delta H_C = -\Delta H_R$**) does not change very much with T thus it will be taken usually at 25°C and 1 atm and it can be function of the standard enthalpy of formation only

$$\Delta H_c = \Delta H_R = H_{Prod} - H_{Reac} \sum N_p h_f^o - \sum N_R h_f^o$$

Where h^o_f is the standard enthalpy of formation of species. The heating value (HV) (KJ/Kmole) of a fuel is the negative of enthalpy of combustion.

$$HV = -\Delta H_C = H_{Reac} - H_{prod}$$

The lower heating value is based on the assumption that the water is in gas form in the products, whereas the higher heating value is based on liquid- phase water in the products. The higher and lower heating values can be calculated from the following relationships:

$$\mathrm{LHV} = H_{\mathrm{Reac}} - H_{\mathrm{Prod},H_2O(g)}$$

and

$$\mathrm{HHV} = H_{\mathrm{Reac}} - H_{\mathrm{Prod},H_2O(l)}$$

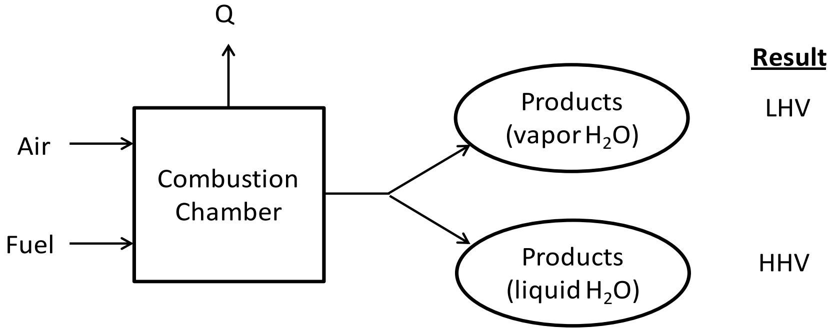
or

$$\mathrm{HHV} = \mathrm{LHV} + (n_{H2O(g)} \text{ in product x } \Delta H_{vap} \text{ of } H_2)$$

where HHV and LHV in (kJ/kmole). ΔH_{vap} is the enthalpy of vaporization of water at 25°C and 1 atm.

Higher (gross) Heating Value (HHV) is the standard heat of combustion of fuel when water (H_2O) in the combustion products is in the form of a liquid.

Lower (net) Heating Value (LHV) is the standard heat of combustion of fuel when water (H_2O) in the combustion products is in the form of a vapour.



Example 1

Determine the higher and lower heating values at 298 K of gaseous methan, CH_4, per kmole of fuel and per kilogram of fuel. The molecular weight of CH_4 is 16 kg/kmole. The standard enthalpies of chemicals used have shown in the table below.

Formula	Standard heat of formation h_f^o (kJ/kg)	Mw (Kg/kmol)	Standard heat of formation h_f^o (kJ/kmole)
CH_4	-4676.94	16	-74831
CO_2	-8944.23	44	-393546
$H_2O(l)$	-15880.94	18	-285857
$H_2O(g)$	-13435.94	18	-241847

Solution

For 1 mole of CH_4, the combustion equation can be written as

$$\mathbf{CH4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O(g\ or\ l)}$$

Higher heating value: $\mathrm{HHV} = \mathrm{H}_{\mathrm{Reac}} - \mathrm{H}_{\mathrm{Prod,H_2O(l)}}$

where $H_{\mathrm{Reac}} = \sum N_i h_i$ and $H_{\mathrm{Prod}} = \sum N_i h_i$,

The enthalpies of formation of the O_2 is also zero at 298 K. Recognizing that we obtain

$$\mathrm{HHV} = \Delta H_{c,\mathrm{H_2O(l)}} = (1)\bar{h}^o_{f,\mathrm{CH_4}} - \left[(1)\ \bar{h}^o_{f,\mathrm{CO_2}} + 2\ \bar{h}^o_{f,\mathrm{H_2O(l)}}\right].$$

$$HHV = (1)\left[-74831\frac{kJ}{kmol}\right] - \left[\left(-393546\frac{kJ}{kmol}\right) + 2\left(-285857\frac{kJ}{kmol}\right)\right]$$

$$HHV = 890429 kJ = \frac{890429 kJ}{1 kmol CH_4} = 890429 kJ / kmole CH_4$$

$$HHV = \frac{890429 kJ / kmole CH_4}{16 kg / kmol} = 55652 kJ / kg CH_4$$

Lower heating value: $\mathrm{LHV} = \mathrm{H}_{\mathrm{Reac}} - \mathrm{H}_{\mathrm{Prod,H_2O(g)}}$

$$\mathrm{LHV} = \Delta H_{c,\mathrm{H_2O}_{(g)}} = (1)\bar{h}^o_{f,\mathrm{CH_4}} - \left[(1)\ \bar{h}^o_{f,\mathrm{CO_2}} + 2\ \bar{h}^o_{f,\mathrm{H_2O}_{(g)}}\right].$$

$$LHV = (1)\left[-74831\frac{kJ}{kmol}\right] - \left[\left(-393546\frac{kJ}{kmol}\right) + 2\left(-241847\frac{kJ}{kmol}\right)\right]$$

$$LHV = 802409 kJ = \frac{802409 kJ}{1 kmol CH_4} = 802409 kJ / kmole CH_4$$

$$LHV = \frac{802409 kJ / kmole CH_4}{16 kg / kmole} = 50151 kJ / kg CH_4$$

Example 2

A natural gas contains 75.1% methane (CH_4) and 24.9% ethane (C_2H_6) by volume. The heats of Combustion (ΔH_C) of methane and ethane at 25 °C and 1 atm with water vapour as the assumed products are given below. The standard heat of vaporization of water is 44.013 kJ/mole. Calculate the HHV (kJ/g) of the natural gas for 1 mole of both: methane and ethane.

Formula	Standard heat of combustion ΔHC (kJ/mole)
CH_4	-802
C_2H_6	-1428

Solution

For 1 mole of CH_4 and I mole of C_2H_6 the combustion equations can be written as

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)} \quad \Delta H_c^\circ = -802 \text{ kJ/mol}$$

$$\mathrm{C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)} \quad \Delta H_c^\circ = -1428 \text{ kJ/mol}$$

$$\begin{aligned}
(HHV)_{CH_4} &= (LHV)_{CH_4} + n_{H_2O}(\Delta\hat{H}_v)_{H_2O} \\
&= \left[802 \frac{\text{kJ}}{\text{mol CH}_4} + \frac{2 \text{ mol H}_2\text{O}}{\text{mol CH}_4}\left(44.013 \frac{\text{kJ}}{\text{mol H}_2\text{O}}\right)\right] \frac{1 \text{ mol}}{16.0 \text{ g CH}_4} \\
&= 55.6 \text{ kJ/g}
\end{aligned}$$

$$\begin{aligned}
(HHV)_{C_2H_6} &= (LHV)_{C_2H_6} + n_{H_2O}(\Delta\hat{H}_v)_{H_2O} \\
&= \left[1428 \frac{\text{kJ}}{\text{mol C}_2\text{H}_6} + \frac{3 \text{ mol H}_2\text{O}}{\text{mol C}_2\text{H}_6}\left(44.013 \frac{\text{kJ}}{\text{mol H}_2\text{O}}\right)\right] \frac{1 \text{ mol}}{30.0 \text{ g C}_2\text{H}_6} \\
&= 52.0 \text{ kJ/g}
\end{aligned}$$

$$\begin{aligned}
HHV &= x_{CH_4}(HHV)_{CH_4} + x_{C_2H_{64}}(HHV)_{C_2H_6} \\
&= [(0.751)(55.6) + (0.249)(52.0) \text{ kJ/g} \\
&= 54.7 \text{ kJ/g}
\end{aligned}$$

Example 3

A natural gas contains 75 % methane (CH_4) and 15 % ethane (C_2H_6) and 10 % propane (C_3H_8) by volume. The heats of Combustion (ΔH_C) of methane, ethane and propane at 25 °C and 1 atm with water liquid as the assumed products are given below. The standard heat of vaporization of water is 44.013 kJ/mole. Calculate the LHV (kJ/g) of the natural gas for 1 mole of each: methane, ethane and propane.

Formula	Standard heat of combustion ΔHC (kJ/mole)
CH_4	-889.6
C_2H_6	-1560
C_3H_8	-2217.6

Solution

HHV (CH_4) = 889.6 **(kJ/mole),** HHV (C_2H_6) = **1560 (kJ/mole),** HHV (C_3H_8) = **2217.6 (kJ/mole),**

HHV = XCH_4 (HHV)CH_4 + XC_2H_6 (HHV) C_2H_6+ XC_3H_8 (HHV) C_3H_8

=(0.75)(889.6/16) + (0.15)(1560/30) + (0.1)(2217.6/44) = 54.54 kJ/g = **54 540** kJ/kg.

$$CH_4 (g) + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$C_2H_6 (g) + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_3H_8 (g) + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

LHV (CH_4) = 889.6-2(44.013) = 801.6 (kJ/mole)/(16) = 50.098 kJ/g = **50 098** kJ/kg.

LHV (C_2H_6) = [1560-3(44.013) = 1427.96 (kJ/mole)/(30) = 47.599 kJ/g = **47 599** kJ/kg.

LHV (C_3H_8) = [2217.6 -4(44.013) = 2041.548 (kJ/mole)/(44) = 46.399 kJ/g = **46 399** kJ/kg.

LHV = XCH4 (LHV)CH4 + XC2H6 (LHV) C2H6+ XC3H8 (LHV) C3H8

= (0.75)(**50 098**) + (0.15)(**47 599**) + (0.1)(**46 399**) = **49 353** kJ/kg