



Plant Processing of Natural Gas



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1 Fundamentals

Natural gas is colorless, shapeless, and odorless in its pure form. It is a fossil fuel consisting primarily of methane with quantities of ethane, propane, butane, pentane, carbon dioxide, nitrogen, helium, and *hydrogen sulfide*. Natural gas is combustible, gives off a great deal of energy, is clean burning, and emits low levels of byproducts into the air. It is an important source of consumer energy used in homes to generate electricity.

The petroleum industry classifies natural gas by its relationship to crude oil in the underground *reservoir*. *Associated gas* is the term used for natural gas that is in contact with crude oil in the reservoir. The associated gas might be a *gas cap* over the crude oil in a reservoir or a solution of gas and oil. *Nonassociated gas* is found in a gas phase in reservoirs without crude oil.

Whether associated or nonassociated, *gas production streams* are highly variable and can contain a wide range of hydrocarbon and nonhydrocarbon components. These streams might include various mixtures of liquids and gases as well as solid materials. There are usually some nonhydrocarbon components including nitrogen, helium, carbon dioxide, hydrogen sulfide, and water vapor present in the stream. Trace amounts of other components, such as mercury, might also be present.

Natural gas processing plants use physical and chemical processes to separate and recover valuable *hydrocarbon* fluids from a gas stream. In the processing plant, all the pipes, containment vessels, steam lines, tanks, pumps, *compressors*, towers, and instruments contain a gas or liquid undergoing some kind of treatment process.

During the processing, the nonhydrocarbon *contaminants* must be handled properly because they affect gas behavior during treatment, impair the efficiency of processing operations, or can damage the processing equipment. For example, the contaminant, liquid mercury, weakens and bonds with the aluminum *heat exchangers* used to produce supercooled fluids. If mercury is not removed from the gas early in the processing phase, it liquefies and collects on the exchanger's surfaces, eventually destroying the heat exchangers.

FLUID PROPERTIES

When there is a pipe, a steam line, a tank, a pump, a compressor, a tower, an instrument, or even a filled sample container in a gas plant, it almost always contains a *fluid*.

What is a fluid? A fluid can be a gas, a liquid, or a solid. A fluid is defined as any substance that flows freely unless restricted or contained by a barrier. Without the ability to assume a shape of its own, a fluid assumes the shape of the container into which it is placed. Both gases and liquids are classified as fluids.

Natural *gas treatment* is based on the reactions of reservoir fluids in physical and chemical processes. Each fluid has a unique set of properties including gravity, solubility, and flammability controlling its response to given stimuli. A gas processing plant operator must determine the specific properties and conditions of its source of oilfield fluids, or *feedstock*, because each one is different. Problems that occur during gas processing come from a fundamental misunderstanding of the specific fluid properties or the physical and chemical laws that determine fluid behavior.

TREATING AND PROCESSING

Plant unit configurations vary depending on the type of components of the feed gas and the final products desired for consumer use (fig. 2.1).



Courtesy of Chevron

Figure 2.1 Gas processing plant

Feed gas from various gas fields enters the gas plant through pipelines and goes through several units of *treating* and processing, as shown in figure 2.2. The main units perform the following functions:

- Remove oil and condensates
- Remove water
- Separate the natural gas liquids from the natural gas
- Remove sulfur and carbon dioxide
- Remove impurities such as mercury, oxygen, and BETX (benzene, ethylbenzene, toluene, and xylenes)

The first treating unit is the feed gas-receiving system and the condensate stabilization system. Condensate is a light hydrocarbon liquid obtained by condensation of hydrocarbon vapors. It consists of varying proportions of propane butanes, pentanes, and heavier components with little or no methane or ethane. The feed gas receiving system separates the feed gas into gases, aqueous liquid, and hydrocarbon liquid for further processing at plant units *downstream* (fig. 2.3).

The condensate stabilization system removes the light components such as methane, ethane, and propane, dissolved in the hydrocarbon liquid from the feed gas reception system (fig. 2.4). Hydrocarbon liquid normally contains a large amount of dissolved light components because of high pipeline pressures. These light components need to be removed to meet condensate product and other downstream processing requirements.

2

Feed Gas Receiving and Condensate Stabilization

3

Dew-Point Control and Refrigeration Systems

PROCESS DESCRIPTIONS

Raw gas comes from production fields through the pipelines to the feed gas receiving unit and condensate stabilization unit. The raw gas then flows to the gas-treating unit and then to a dew-point control and refrigeration unit or a *natural gas liquid (NGL)* recovery unit. An export compression system is sometimes used after the dew-point control unit to pressurize the gas to the requirements of the *pipeline grid*. Finally, the gas is sent to the consumers through a pipeline grid.

A dew-point control unit helps to prevent liquid condensation in the pipeline grid under various pressures and temperature conditions. There are two kinds of dew-point control required: a *water dew-point control* and a *hydrocarbon dew-point control*. In water dew-point control, there are several dehydration, or water removal, methods available, including the *silica gel*, glycol, and *molecular sieve*. Hydrocarbon dew-point control also has various methods available including refrigerated *low-temperature separation (LTS)*, *expander*, *Joule-Thomson (J-T)*, and silica gel. Companies might use glycol gas dehydration for water dew-point control and a refrigeration cooling system for hydrocarbon dew-point control. More explanation of gas dehydration is given in Chapter 6.

The purpose of a *refrigeration system* is to remove heat from the feed stream in a heat exchanger. Heat exchangers are referred to as *evaporators* or *chillers* and provide the required cooling level for various gas processing applications. Refrigeration systems use refrigerant, called *working fluid*. Working fluid is selected based upon temperature requirements, availability, economics, and previous experience. The availability of ethane and propane on hand at natural gas processing plants makes these gases the prime choice as working fluids. In gas plants, propane is normally the preferred refrigerant.

COST ESTIMATE

Dew-point depression is defined as the difference in degrees between the feed gas temperature and the dew point of a fluid. The dew-point depression difference in degrees determines the best process to use for dew-point control.

Depending on the amount of dew-point depression required, an economic evaluation is done to compare installation costs and operating costs for the various processes. Using an average 80°F (45°C) dew-point depression requirement, there are several processes available for the dew-point control. Three of the most widely used process options are the silica gel process, the glycol/propane refrigeration process, and the glycol/J-T valve cooling process.

4 Hydrocarbon Treating

GAS-TREATING PROCESSES

Hydrocarbon streams, both gaseous and liquid, might contain contaminants such as H_2S and CO_2 that must be removed before further processing and marketing. Removal of H_2S , CO_2 , and other sulfur compounds, commonly called *acid gases*, is normally referred to as hydrocarbon treating or *sweetening*.

Treated gas regulations and specifications are stringent regarding residual H_2S and other sulfur species. Typical U.S. sales gas contracts restrict the following:

H_2S	< 0.25 grains/100 scf (about 4 ppmv)
Total sulfur compounds	< 5 grains/100 scf (about 80 ppmw)
CO_2	< 2 % mole

Acid gas components can be removed from a sour gas stream by:

- chemical reaction using liquids or solids;
- physical *absorption* in liquids;
- adsorption on solids;
- diffusion through membranes.

The acid gas removal processes can be *nonregenerative* or *regenerative*. The nonregenerative processes are suitable only when trace amounts of contaminants must be removed and/or very high purity of treated gas is desired. Nonregenerative processes become too costly when the H_2S to be removed exceeds about 1 ton per day. Examples of nonregenerable treating processes are SulfaTreat® and Chemsweet®, both marketed by C.E. Natco.

Regenerative processes are more economical for removing larger quantities of contaminants. An example of a regenerative process is the use of an aqueous amine solution to remove the H_2S and CO_2 from a sour gas stream. The amine solution is then regenerated by reducing its pressure and heating it to about 250°F. The solution is then cooled and recycled for reuse. Regenerative treating processes can be broadly classified as those that depend on:

- chemical reaction in
 - amine-based solvents,
 - nonamine based solvents;
- physical absorption;
- mixed chemical/physical absorption;
- adsorption on a solid.

CHEMICAL REACTION

In these processes, H_2S and/or CO_2 are chemically bound to the active ingredient in the treating solution. Therefore, the residue gas can be treated to retain only very low levels of these contaminants. The chemical solvent processes in current commercial processes use weak bases like *alkanolamines*, *alkali salt* solutions, *potassium carbonate*, or a *chelate* solution.

5 Sulfur Recovery and Claus Off-Gas Treating

SULFUR RECOVERY

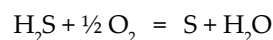
Gas treating plants must strictly comply with legal, government, and safety standards and regulations concerning emissions and pollution. During the treatment process, H₂S and some or most of the CO₂ are removed from the sour gas stream, as discussed in Chapter 4. These removed sour gas components must be dealt with cautiously.

While the emissions requirements vary with geography, most countries do not permit the emission of more than a few pounds of sulfur (H₂S, SO₂, etc.) per day into the atmosphere. To control emissions, the acid gas stream from a treating plant is fed to a sulfur recovery unit (SRU) where H₂S and other sulfur compounds are converted and recovered as nontoxic elemental sulfur (S). The tail gas from the SRU still contains some sulfur components. These are converted to SO₂ in an incinerator before being discharged into the atmosphere. If high (99.8+%) sulfur recovery is desired, the SRU tail gas is fed to a tail-gas treating plant for further reduction of sulfur emissions.

Thermal Process

In 1883, an English scientist, Carl Friedrich Claus, discovered and patented a process in which H₂S was reduced to elemental sulfur and water in the presence of a catalyst.

Claus's formula for this process is:



The control of this *exothermic*, or heat-releasing, process was difficult, and conversion to elemental S was low. The modified Claus process used today overcomes the control and conversion problems by dividing the Claus process into the following two steps:

Thermal Step

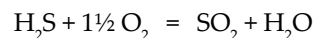
In this exothermic step, the air-to-acid gas ratio is controlled so that about N of the H₂S is oxidized to SO₂. For gases containing hydrocarbons and/or ammonia from a sour water stripper, enough air is injected to ensure complete combustion of ammonia and hydrocarbon components. The process temperature during this step is from 1,800°F–2,500°F.

Catalytic Step

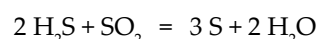
In this moderately exothermic catalytic reaction, the sulfur dioxide (SO₂) formed in the thermal section reacts with unburned H₂S to form gaseous elemental sulfur. The catalyst used in this step is made from activated alumina or titanium dioxide.

Other than the reactions of hydrocarbons and other combustibles, the key reactions taking place are:

Thermal Reaction:



Thermal and Catalytic Reaction:



DEHYDRATION

All hydrocarbon fluids can retain some water. Water is soluble in liquid hydrocarbons and can be held in the vapor phase by hydrocarbon gases. When a liquid or gas is cooled, its capacity for containing water decreases. As a result, it can produce liquid and/or solid water called hydrates. Hydrates are a separate and problematic part of gas processing.

Figure 6.1 shows how the water content of natural gas varies with temperature and pressure. For example, at 1,000 psia and 100°F, water-saturated natural gas contains about 62 pounds of water per million standard cubic feet (MMscf) of gas. At 1,000 psia and 0°F, the gas contains only about 2 pounds of water per MMscf of gas.

The water dew point of a gas or liquid is the temperature at which free water will begin to separate from the gas or liquid. If a natural gas stream at 1,000 psia contains 62 pounds of water per MMscf of gas, its water dew point is 100°F. If it is cooled below 100°F, free water will be present.

Hydrates will form if a gas or liquid containing free water is cooled below its hydrate temperature. The graph shown in figure 6.2 can be used to estimate the hydrate temperature of natural gas. For instance, a 0.6 specific gravity gas has a hydrate temperature of about 61°F at 1,000 psia. If this gas must be cooled below its hydrate temperature, either due to pipeline transportation, pressure reduction for consumption, or for processing, precautions must be taken to prevent free-water dropout that causes freezing and formation of hydrates.

Hydrates are solid compounds that form as crystals and resemble snow. They are created by a reaction of natural gas with water, and when formed, are about 10% hydrocarbon and 90% water. Hydrates have a specific gravity of about 0.98 and will float in water and sink in hydrocarbon liquids. Freezing can be avoided by either removing the water from the gas or liquid prior to cooling below the hydrate temperature or by using a hydrate inhibitor to mix with the water condensed during cooling.

Dehydration is the process of removing water from a substance. Dehydration can be accomplished by using solid substances such as those used in dry-bed dehydrators. It can also be done using a liquid, such as triethylene glycol. A *stripping gas* in a TEG reboiler can also be used. The more common hydrate inhibitors are methanol and ethylene glycol. Most natural gas facilities use one or more of the following dehydration processes: ethylene glycol injection, TEG dehydration, or dry-bed dehydrators.

6 Dehydration and Mercury Removal

Straight from the well, natural gas is a mix of hydrocarbons, including methane, ethane, propane, and butane. It also contains many nonhydrocarbons, such as nitrogen, helium, carbon dioxide, hydrogen sulfide, and water. Raw gas is processed to separate these components. These processes continue to improve with advanced technology.

Previously, when kerosene was a highly valued product and natural gas was simply an unwanted byproduct, most natural gas was wasted. Gas was commonly flared off—a process that often continued day and night. Little was done to capture any gas products. A few operators put traps in their lines to catch *drip gas*. A form of gasoline, drip gas naturally condenses as it comes from the natural gas wells and cools in field-gathering lines.

Gasoline began to surpass kerosene sales around 1912. The first gas processors learned to increase the yield of drip gas by compressing the gas and allowing it to cool. With the demand for fuel gasoline growing quickly, producers began trying to get more usable products from the oil and gas. An increased-yield process, called *lean oil absorption*, was developed in the 1920s. Lean oil is a hydrocarbon liquid, usually lighter than kerosene. In contact with natural gas, lean oil absorbs some of the heavier hydrocarbons from the gas, which can be separated from the oil later. Using this process, operators recovered more gas condensate as well as butane, a gas that liquefies easily under pressure. This was the beginning of the NGL market.

In the 1950s, processors improved the yield from lean-oil absorption by adding refrigeration to the process. Advancing technology has added the development of better refrigeration equipment, lower processing temperatures, and new ways to market natural gas.

Lean-oil absorption is only one of many ways to separate the various products in natural gas. Instead of using lean-oil absorption, plants might use a less expensive process by refrigerating the gas to remove the propane and heavier hydrocarbons. Many of the newest gas processing plants only produce a single NGL product called Y-grade, which is then shipped to another plant for further separation.

Chapter 7 presents the older, but still commonly used, lean-oil absorption process. Chapter 8 covers the newer processes of refrigeration and *turboexpansion*. However, the complete range of process possibilities cannot be fully explored in these chapters because gas plants often use combinations and modified versions of these processes, depending on the range of products produced.

7 NGL Recovery— Lean-Oil Absorption

8 NGL Recovery- Cryogenic

The heavier hydrocarbons, generally referred to as NGLs, might need to be removed to control the hydrocarbon dew point and/or the gas heating value. However, heavier hydrocarbons can also be a source of income for the gas producer. The history of the evolution of liquids recovery facilities from simple oil absorption to cryogenic expander processes is complex (Elliot, 1996).

Lean-oil absorption processes, such as the ambient and refrigerated processes, were commonly used until the early 1970s, as shown in figure 8.1.

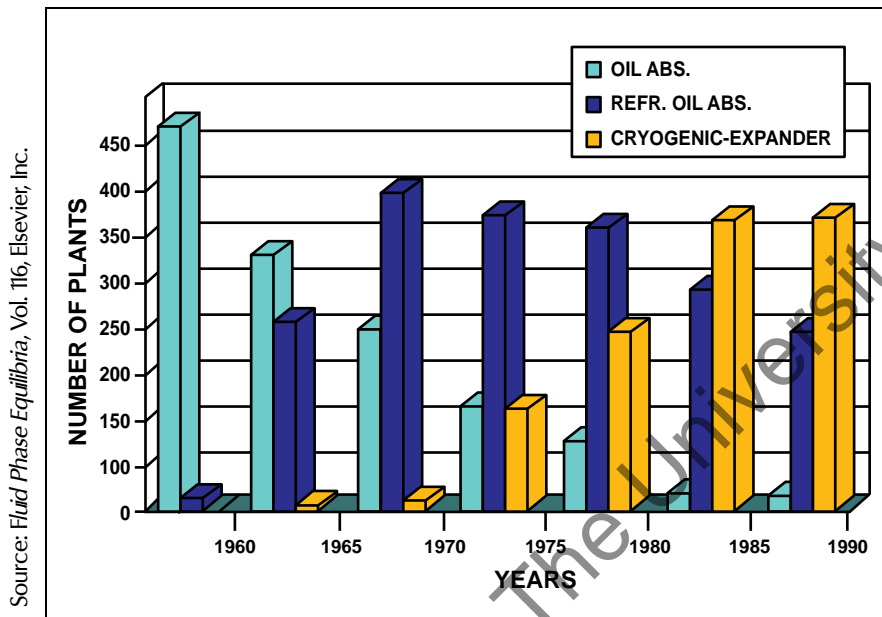


Figure 81 Lean-oil absorption process and cryogenic process

The refrigerated oil absorption process was introduced in 1957 by modifying the ambient oil absorption process to operate at lower temperatures. This allowed the use of lower molecular weight oils which recover more NGLs than the higher molecular weight oils, used in the ambient process. At a temperature of -40°F, the refrigerated oil absorption process could be used to recover up to 40+% ethane and 90+% propane in the feed gas.

A major shift in the gas processing industry began when the first low-temperature expander plant was built and brought into operation in 1964. The basic design of this plant remains today. During the 1970s, the expander plant became the dominant process scheme used to recover NGLs from feed gas. It is an efficient process for high ethane and propane recovery.

FRACTIONATION

The basis for most hydrocarbon phase separations is the equilibrium flash process. A flash process gives a “sloppy” or imprecise separation of the components in a mixture. The liquid and vapor phases of the flash process still contain all the components that were present in the feed gas. To better separate the feed components, a process called fractionation, or distillation, was developed. Fractionation is possible when the components to be separated have different boiling points. The higher the difference in the boiling points, the easier it is to separate the components.

During fractionation, a mixture is separated into individual components or groups of components. Fractionation is a *countercurrent operation* in which vapor mixtures are repeatedly brought in contact with liquid mixtures having similar composition as the vapors. The liquids are at their *bubble points* and the vapors are at their dew points. Bubble point is the temperature at which the first bubble of gas forms in liquid. Part of the vapor condenses, and part of the liquid vaporizes during each contact. The vapor becomes richer in the lighter or lower boiling components, and the liquid becomes richer in the heavier or higher boiling components.

A fractionating column can be viewed as a combination of absorption and stripping columns. Figure 9.1 is a schematic diagram of a fractionation column with the associated and peripheral equipment.

The cooling in a condenser is done either by air, cooling water, or a refrigerant such as propane. The column pressure normally determines the cooling medium that is used. Reboiler heat is provided by steam, hot oil, hot medium fluids, hot compressor discharge gas, or a hot process stream.

The number of trays or the height of the packed section in a fractionation column depends upon the number of vapor/liquid contacts required to make the desired separation. Fractionation columns use *valve trays* with *downcomers* or pipes that move the liquid from one tray to the one below. The valves open either partially or fully by vapor flowing through the tray. A *weir* maintains liquid level on the tray. Liquid flows across the tray, over the weir, and through a downcomer or down pipe to the tray below. Large-diameter columns might have two or four liquid flow-passes on each tray. Figure 9.2 shows flow through vapor passages on a tray in a fractionation column.

9

Fractionation and Liquid Treating

10

Nitrogen Rejection Unit (NRU)

NITROGEN REJECTION

Nitrogen (N_2) is an inert gas found in varying amounts in natural gas reservoirs. *Nitrogen rejection* is a necessary process in maintaining a desired Btu value for sales gas and pipeline specifications. Nitrogen is added to or removed from the sales gas to adjust its heating or Btu value. Adding nitrogen lowers the Btu value, while removing nitrogen raises the Btu value. However, there is a limit to the maximum amount of N_2 or inert gases allowed. Nitrogen has an additional use in the *enhanced oil recovery* (EOR) processes and for increasing oil production through reservoir injection.

Nitrogen is removed from the feed gas at low temperatures in a *nitrogen rejection unit (NRU)* designed according to:

- Inlet gas composition
- Inlet gas pressure
- Product specifications
- Vent nitrogen
- Residue gas heating value
- Hydrocarbon recovery required

NRUs operate best under stable compositions, inlet rates, temperatures, and pressures, and must be designed to efficiently operate over a broad range of nitrogen gas compositions (5%–80%). The quantity of nitrogen in the feed gas is generally the main factor in selecting a nitrogen removal process.

NRU PROCESS SELECTION

There are four categories of processes currently available for removal of nitrogen from natural gas.

Pressure Swing Adsorption (PSA)

Pressure swing adsorption is a technology used to separate nitrogen under pressure according to its molecular characteristics and attraction to an adsorbent material at near-ambient temperatures. Special adsorptive materials are used as a molecular sieve, adsorbing the hydrocarbon components at high pressure. The process then swings to low pressure to desorb the adsorbent material. Methane is produced during the desorption step at relatively low pressure near ambient or under vacuum in some cases. It often requires pretreatment and has high capital and compression costs. The recovery of methane is generally moderate.

Cryogenic Absorption

The *cryogenic absorption process* uses chilled hydrocarbon oil to absorb the bulk of the methane and achieve a separation of nitrogen from natural gas. The absorbed methane is stripped off the oil in a regenerator and subsequently compressed back to the pipeline pressure. The need to absorb the bulk of methane requires a large oil circulation flow and equipment size. Therefore, it is most suitable for high nitrogen content streams. It has not been widely used commercially.

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