

*University of Technology
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4th Year/Oil and Gas Refinery Eng.*



*Lectures in
Gas Technology
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Gas Technology

Syllabus:

- ✦ Introduction to Natural Gas Industry, Gas Glossary.*
- ✦ Gaseous fuels: Classification & Advantages.*
- ✦ Natural Gas Fundamentals: NG History, NG Origin & Composition.*
- ✦ Gas Sources, Phase Behavior of NG, NG Properties.*
- ✦ Basic Concepts of Natural Gas Processing.*
- ✦ Condensate Stabilization.*
- ✦ Sweetening Processes: Amine Process, Sulfinol Process, Design Aspects.*
- ✦ Natural Gas Dehydration: Absorption Processes, Adsorption processes, Design Aspects.*
- ✦ Separation of Natural Gas Liquids*
- ✦ Gas to Liquids Technology*

References:

- 1)** Campbell, J.M., “Gas Conditioning and Processing,” 3rd Ed. Campbell, (1992).
- 2)** Saeid Mokhatab S. & William A. Poe, "Natural Gas Transmission and Processing" (2006).
- 3)** Abdel Aal H.K. , Mohamed Aggour and Fahim M. K.," Petroleum and Gas Field Processing", (2003).
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Lecture (1)

DEFINITIONS

Natural gas is the gas obtained from natural underground reservoirs either as free gas or gas associated with crude oil. It generally contains large amounts of methane (CH_4) along with decreasing amounts of other hydrocarbons. Impurities such as H_2S , N_2 , and CO_2 are often found with the gas. It also generally comes saturated with water vapor.

Pipeline Gas is the gas which has the quality to be used as a domestic or industrial fuel. It meets the specifications set by a pipeline transmission company, and/or distributing company.

Sour Gas: Gas that contains more than 1 grain of H_2S /100 SCF

Sweet Gas: Gas in which the H_2S content is less than 1 grain /100 SCF.

Wet Gas: Gas that contains more than 0.1 US gallons of condensates per 1000 CF of gas.

Dry Gas: Gas that contains less than 0.1 US gallons of condensates per 1000 CF of gas.

Rich Gas: Gas containing more than 5 to 7 US gallons of compounds heavier than ethane (C_3^+) per 1000 CF of the gas.

Lean Gas: Gas containing 1 US gallons or less of compounds heavier than ethane (C_3^+) per 1000 CF of the gas.

Pentanes⁺: The pentane and heavier fraction of hydrocarbon liquid.

Condensates: The hydrocarbon liquid fraction obtained from a gas stream containing essentially pentanes.

Liquefied natural gas (LNG):

- When natural gas is cooled to a temperature of approximately $-260\text{ }^\circ\text{F}$ ($-160\text{ }^\circ\text{C}$) at atmospheric pressure it condenses to a liquid called liquefied natural gas (LNG).
- One volume of this liquid takes up about 1/600th the volume of natural gas at a stove burner tip.
- LNG is only about 45% the density of water.
- LNG is odorless, colorless, non-corrosive, and non-toxic.
- When vaporized it burns only in concentrations of 5% to 15% when mixed with air.
- Neither LNG, nor its vapor, can explode in an unconfined environment.

Compressed natural gas (CNG):

- Is natural gas pressurized and stored in welding bottle-like tanks at pressures up to 3,600 psig (25 MPa).
- Typically, it is same composition of the local "pipeline" gas, with some of the water removed.

Liquid petroleum gas (LPG):

- Sometimes called **propane** is often confused with LNG and vice versa. They are not the same and the differences are significant.
- Varieties of LPG bought and sold include mixes that are primarily propane, mixes that are primarily **butane**, and mixes including propane, propylene, n-butane, butylene and iso-butane.
- Depending on the season—in winter more propane, in summer more butane. Vapor pressures, at 30°C, are for commercial propane in the range 10-12 barg (1 to 1.2 MPa), for commercial butane, 2-4 barg (0.2 to 0.4 MPa). In some countries LPG is composed primarily of propane (upwards to 95%) and smaller quantities of butane.

LPG compared to natural gas

1. Has a significantly higher heating value
2. Requires a different air-to-gas mixture (propane: 24:1, butane: 30:1) for good combustion.
3. LPG can be stored as a liquid in tanks by applying pressure alone. While the distribution of LNG requires heavy infrastructure investments (pipelines, etc.), LPG is portable. This fact makes LPG very interesting for developing countries and rural areas.

LPG (sometimes called autogas) has also been used as fuel in light duty vehicles for many years. An increasing number of petrol stations around the world offer LPG pumps as well. A final example that should not be forgotten is that the "bottled gas" can often be found under barbecue grills.

Lecture (2)

GASEOUS FUELS

Classification of Gaseous Fuels

The following is a list of the types of gaseous fuel:

(A) Fuels naturally found in nature:

- Natural gas
- Methane from coal mines

(B) Fuel gases made from solid fuel

- Gases derived from Coal
- Gases derived from waste and Biomass
- From other industrial processes (Blast furnace gas)

(C) Gases made from petroleum

- Liquefied Petroleum gas (LPG)
- Refinery gases
- Gases from oil gasification

(D) Gases from some fermentation processes.

The Importance of Gaseous Fuels

- Generally VERY clean burning. Little soot. Operate with low XSA.
- Easy to burn - No grinding or atomization. Excellent mixing
- No problems with erosion or corrosion
- No ash
- The gas is easy to clean. E.g. if sulfur is present, it may be easily removed prior to combustion.
- Simplest combustion plant of all { Burners, Control system, No ash problems, Heat exchangers, Can be started up and shut down very easily and quickly}.

Disadvantages of gaseous fuels

- Problems with distribution and storage
- Explosion risk - very volatile.
- Relatively costly. Offset by cheaper and more efficient plant.

Natural Gas Fundamentals

Origin & Composition

Natural gas is a fossil fuel source of energy, which represents more than one fifth of total energy consumption in the world. It has been the fastest growing fossil fuel since the seventies.

Natural gas is used primarily as a ***fuel and as a raw material in manufacturing***.

- It is used in home furnaces, water heaters, and cooking stoves. As an industrial fuel, it is used in brick, cement, and ceramic-tile kilns; in glass making; for generating steam in water boilers; and as a clean heat source for sterilizing instruments and processing foods.
- As a raw material in petrochemical manufacturing. Ethylene, an important petrochemical, is produced from natural gas.
- Natural gas is used to produce hydrogen, sulfur, carbon black, and ammonia. The ammonia is used in a range of fertilizers and as a secondary feedstock for manufacturing other chemicals, including nitric acid and urea.

Natural gas is considered as ***an environmentally friendly clean fuel***, offering important environmental benefits when compared to other fossil fuels.

Natural gas exists in nature under pressure in rock reservoirs in the Earth's crust, either in conjunction with and dissolved in heavier hydrocarbons and water or by itself. It is produced from the reservoir similarly to or in conjunction with crude oil. Natural gas has been formed by the degradation of organic matter accumulated in the past millions of years. Two main mechanisms (***biogenic and thermogenic***) are responsible for this degradation

- ***Biogenic gas*** is formed at shallow depths and low temperatures by the anaerobic bacterial decomposition of sedimentary organic matter. Biogenic gas consists almost entirely of methane.

Methanogens are microscopic organisms which live in environments devoid of oxygen and chemically decompose organic matter, creating methane as a byproduct.

- ***Thermogenic gas*** is formed at deeper depths by:

- (1) Thermal cracking of sedimentary organic matter into hydrocarbon liquids and gas
- (2) Thermal cracking of oil at high temperatures into gas.

Thermogenic gas can also contain significant concentrations of ethane, propane, butanes, and heavier hydrocarbons.

Natural Gas Resources

The presence of gas in a mixture of hydrocarbons depends on their phase behavior, which in turn, depends greatly on

- The pressure and temperature of the mixture which both increase with depth
- The history of the reservoir.

It is generally true that ***the same organic matter could have evolved into***

- ***Coal,***
- ***Heavy oil with virtually no gas, usually found at depth \leq 3000ft***
- ***Light oil with lots of dissolved gas, at depths $>$ 3000ft Oil becomes lighter which means that gas coexist with oil.*** Gas can be in the form of :
 - ➡ A ***gas-cap*** on top of the oil zone, or
 - ➡ It can be dissolved in the oil.

As depth increases, more gas is present. Around 10,000 to 12,000 ft depth are some of the most prolific oil reservoirs in the world and almost all of them contain oil of API gravity between 28 and 32. They also coexist with substantial quantities of gas, which, when separated from oil at the surface, will evolve into 500 to 1,000 scf/stb (standard cubic feet per stock tank barrel).

- ***Just gas.*** At depth of 17,000 ft and certainly over 20,000 ft, reservoirs contain almost exclusively natural gas.

[Terms used in the petroleum industry to describe natural gas reservoirs]

Associated gas is produced with the oil and separated at the casinghead or wellhead. Gas produced in this fashion is also referred to as *casinghead gas*, *oil well gas*, or *dissolved gas*.

Nonassociated gas is sometimes referred to as *gas-well gas* or *dry gas*. However, this dry gas can still contain significant amounts of NGL components.

Gas condensate reservoirs, occurs where, because of the high pressures and temperatures, the material is present not as a liquid or a gas but as a very dense, high-pressure fluid.

Figure (1) shows a simplified flow of material from reservoir to finished product and provides an overall perspective of the steps involved in taking natural gas from the wellhead to the customer. Some gas plants receive feeds from refineries. These streams differ from natural gases in that they can contain propylene and butylene. They may also contain trace amounts of undesirable nitrogen compounds and fluorides.

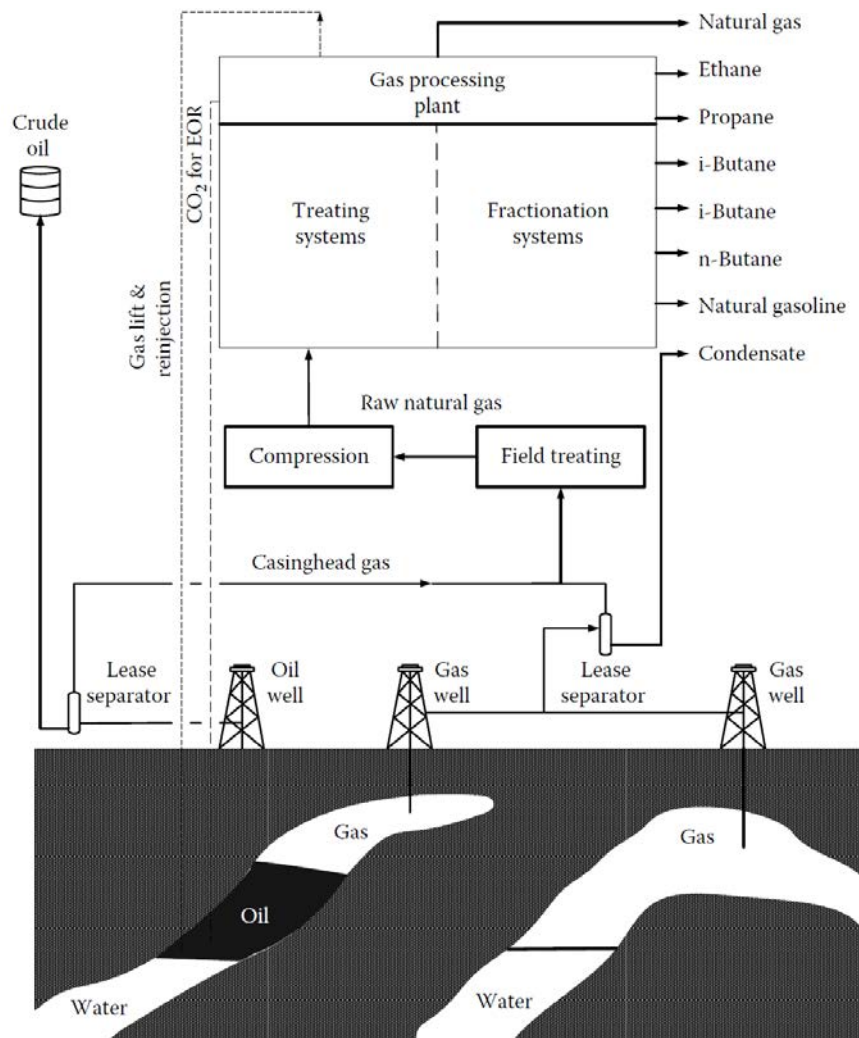


Figure 1: Schematic Overview of Natural Gas Industry

Composition of natural gas

Raw natural gas typically consists primarily of methane (CH_4), the shortest and lightest hydrocarbon molecule. It also contains varying amounts of:

- ❖ Heavier gaseous hydrocarbons: ethane (C_2H_6), propane (C_3H_8), normal butane ($n\text{-C}_4\text{H}_{10}$), iso-butane ($i\text{-C}_4\text{H}_{10}$), pentanes and even higher molecular weight hydrocarbons. When processed and purified into finished by-products, all of these are collectively referred to *NGL (Natural Gas Liquids)*.
- ❖ *Acid gases*: carbon dioxide (CO_2), hydrogen sulfide (H_2S) and mercaptans such as methanethiol (CH_3SH) and ethanethiol ($\text{C}_2\text{H}_5\text{SH}$).
- ❖ Other gases: nitrogen (N_2) and helium (He).
- ❖ Water: water vapor and liquid water.
- ❖ Liquid hydrocarbons: perhaps some natural gas condensate (also referred to as *casing-head gasoline or natural gasoline*) and/or crude oil.
- ❖ *Mercury*: very small amounts of mercury primarily in elementary form, but chlorides and other species are possibly present.

Natural gas is considered “*dry*” when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is “*wet*”. The composition of natural gas varies depending on the field, formation, or reservoir from which it is extracted.

Table 1: Typical Composition of Natural Gas

| Name | Formula | Volume (%) |
|------------------|---------------------------|------------|
| Methane | CH_4 | >85 |
| Ethane | C_2H_6 | 3–8 |
| Propane | C_3H_8 | 1–2 |
| Butane | C_4H_{10} | <1 |
| Pentane | C_5H_{12} | <1 |
| Carbon dioxide | CO_2 | 1–2 |
| Hydrogen sulfide | H_2S | <1 |
| Nitrogen | N_2 | 1–5 |
| Helium | He | <0.5 |

Gas Specifications and Standard Conditions

Market sales of natural gas require some specifications set by the consumers regarding the maximum contents allowable for the following: acidic gases and sulfur, oxygen and carbon dioxide, water vapor, and liquefiable hydrocarbons. The thermal heating content of the gas sets another value to be met as a minimum. ***In general, the standards specify that the natural gas:***

- Be within a specific range of heating value (caloric value). For example, in the United States, it should be about $1,035 \pm 5\%$ Btu per cubic foot of gas at 1 atmosphere and 60 °F ($41 \text{ MJ} \pm 5\%$ per cubic metre of gas at 1 atmosphere and 0°C).
- Be delivered at or above a specified hydrocarbon dew point temperature (below which some of the hydrocarbons in the gas might condense at pipeline pressure forming liquid slugs which could damage the pipeline).
- Be free of particulate solids and liquid water to prevent erosion, corrosion or other damage to the pipeline.
- Be dehydrated of water vapor sufficiently to prevent the formation of methane hydrates within the gas processing plant or subsequently within the sales gas transmission pipeline.
- Contain no more than trace amounts of components such as hydrogen sulfide, carbon dioxide, mercaptans, nitrogen, and water vapor.
- Maintain mercury at less than detectible limits (approximately 0.001 ppb by volume) primarily to avoid damaging equipment in the gas processing plant or the pipeline transmission system from mercury amalgamation and embrittlement of aluminum and other metals

Irrespective of the source of natural gas, the final specifications set for market sales requirements are usually as given in table 2:

Table 2: Natural Gas Market Sales Requirements

| | |
|--------------------------|--|
| H ₂ S | 0.25–0.3 grain per 100ft ³ (one grain = 64.799 mg) |
| Total sulfur | 20 grains per 100 ft ³ |
| Oxygen (air) | 0.2% by volume |
| Carbon dioxide | 2% by volume |
| Liquefiable hydrocarbons | 0.2 gal per 1000 ft ³ |
| Water content | 7 lbs/MMSCF (in a 1000-psia gas line) |
| Thermal heating value | 1150 Btu/ft ³ |

As for the standard conditions used in the gas industry for reporting the volumetric properties of the gas, two common standard conditions of temperature and pressure are used:

1. *Universal scientific, reported at 32°F and 760mmHg*

2. *Natural gas industry, reported at 60°F and 14.7 psia*

Under the universal standard conditions, for an ideal gas, the following is applied:

1 g mole occupies 22.4 liters

1 kg mole occupies 22.4 cubic meters

1 lb mole occupies 359 cubic feet

Effect of Impurities Found in Natural Gas

Field processing operations of natural gas, which is classified as a part of gas engineering, generally include the following:

1. *Removal of water vapor, dehydration*

2. *Removal of acidic gases (H₂S and CO₂)*

3. Separation of heavy hydrocarbons

The effect of each of these impurities has on the gas industry, as end user, is briefly outlined in table 3:

Table 3: Effect of Impurities on Gas Industry

| Water vapor | H ₂ S and CO ₂ | Liquid hydrocarbons |
|--|--|--|
| It is a common impurity. It is not objectionable as such. | Both gases are harmful, especially H ₂ S, which is toxic if burned; it gives SO ₂ and SO ₃ which are nuisance to consumers. | Their presence is undesirable in the gas used as a fuel. |
| (a) Liquid water accelerates corrosion in the presence of H ₂ S gas. | <ul style="list-style-type: none"> Both gases are corrosive in the presence of water. | <ul style="list-style-type: none"> The liquid form is objectionable for burners designed for gas fuels. |
| (b) Solid hydrates, made up of water and hydrocarbons, plug valves, fittings in pipelines, and so forth. | <ul style="list-style-type: none"> CO₂ contributes a lower heating value to the gas. | <ul style="list-style-type: none"> For pipelines, it is a serious problem to handle two-phase flow: liquid and gas. |

Natural Gas Phase Behavior

The natural gas phase behavior is a plot of pressure vs. temperature (Figure 2) that determines whether the natural gas stream at a given pressure and temperature consists of a single gas phase or two phases: gas and liquid.

- ✚ **Bubble Point Curve**—the curve that separates the pure liquid (oil) phase from the two-phase (natural gas and oil) region. This means that at a given temperature, when pressure decreases and below the bubble point curve, gas will be emitted from the liquid phase to the two-phase region.
- ✚ **Dew Point Curve**—the curve that separates the pure gas phase from the two-phase region. It is the connected points of pressure and temperature at which the first liquid droplet is formed out of the gas phase.
- ✚ **Critical Point**—the point on the phase envelope where the bubble point curve meets the dew point curve. At that given pressure and temperature, gas properties are identical to liquid properties. The pressure and temperature at the critical point are called critical pressure and temperature, respectively.
- ✚ **Cricondentherm**—the highest temperature at which liquid and vapor can coexist. That means the mixture will be gas irrespective of pressure when the temperature is larger than cricondentherm.
- ✚ **Cricondenbar**—the highest pressure at which a liquid and vapor can coexist.

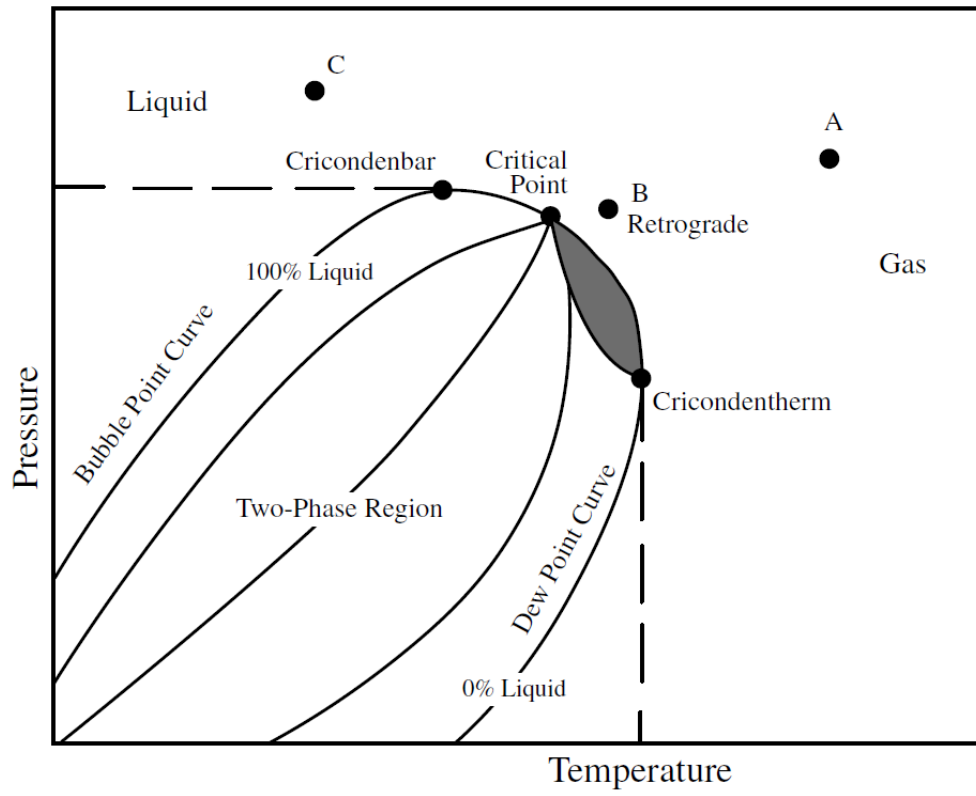


Figure 2: Pressure-Temperature Diagram for A Typical Natural Gas Mixture

Lecture (3)

NATURAL GAS PROPERTIES

Chemical and Physical Properties

Natural gas is colorless, odorless, tasteless, shapeless, and lighter than air. The natural gas after appropriate treatment for acid gas reduction, odorization, and hydrocarbon and moisture dew point adjustment would then be sold within prescribed limits of pressure, calorific value, and possibly **Wobbe index** (often referred to as the **Wobbe number**).

The Wobbe index (calorific value divided by the specific gravity) gives a measure of the heat input to an appliance through a given aperture at a given gas pressure.

Table 4: 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, 15°C | 0.72–0.81 |
| Boiling point, °C | –162 |
| Autoignition temperature, °C | 540–560 |
| Octane number | 120–130 |
| Methane number | 69–99 |
| Stoichiometric air/fuel ratio, weight | 17.2 |
| Vapour 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 |
| Carbon dioxide concentration, volume % | 1–5 |
| Sulfur concentration, weight % ppm | <5 |
| Specific CO ₂ formation, g/MJ | 38–50 |

Gas-Specific Gravity

Specific gravity of gas is defined as

$$\gamma_g = \frac{M}{M_{\text{air}}} \text{-----(1)}$$

Where M_{air} is the molecular weight of air, which is equal to 29. Once we can calculate the value of the molecular weight of the mixture, we can calculate the specific gravity of the mixture. For a gas mixture, we can calculate the molecular weight as

$$M = \sum_{i=1}^n y_i M_i$$

------(2)

Where M_i is the molecular weight of component i , y_i is the mole fraction of component i , and n is the total number of components.

Ideal and Real Gas Laws

$$PV = ZnRT$$

$$P_r = \frac{P}{P_c} \text{ and } T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c} \text{ and } T_r = \frac{T}{T_c}$$

$$P_c = \sum_i^n P_{ci} y_i \text{ and } T_c = \sum_i^n T_{ci} y_i$$

The Z factor chart of Standing and Katz (1942) , Shown in figure (3) is only valid for mixtures of hydrocarbon gases.

Wichert and Aziz (1972) developed a correlation to account for inaccuracies in the Standing and Katz chart when the gas contains significant fractions of acid gases, specifically carbon dioxide (CO_2) and hydrocarbon sulfide (H_2S). The Wichert and Aziz (1972) correlation modifies the values of the pseudocritical temperature and pressure of the gas. Once the modified pseudocritical properties are obtained, they are used to calculate pseudo-reduced properties and the Z factor.

The Wichert and Aziz (1972) correlation first calculates a deviation parameter ϵ :

$$\epsilon = 120(A^{0.9} - A^{1.6}) + 15(B^{0.5} - B^4)$$

where A is the sum of the mole fractions of CO_2 and H_2S in the gas mixture and B is the mole fraction of H_2S in the gas mixture. Then, ϵ is used to determine the modified pseudocritical properties as follows:

$$T'_{pc} = T_{pc} - \epsilon$$

$$P'_{pc} = \frac{P_{pc} T'_{pc}}{[T_{pc} - B(1 - B)\epsilon]}$$

The correlation is applicable to concentrations of $\text{CO}_2 < 54.4 \text{ mol\%}$ and $\text{H}_2\text{S} < 73.8 \text{ mol\%}$.

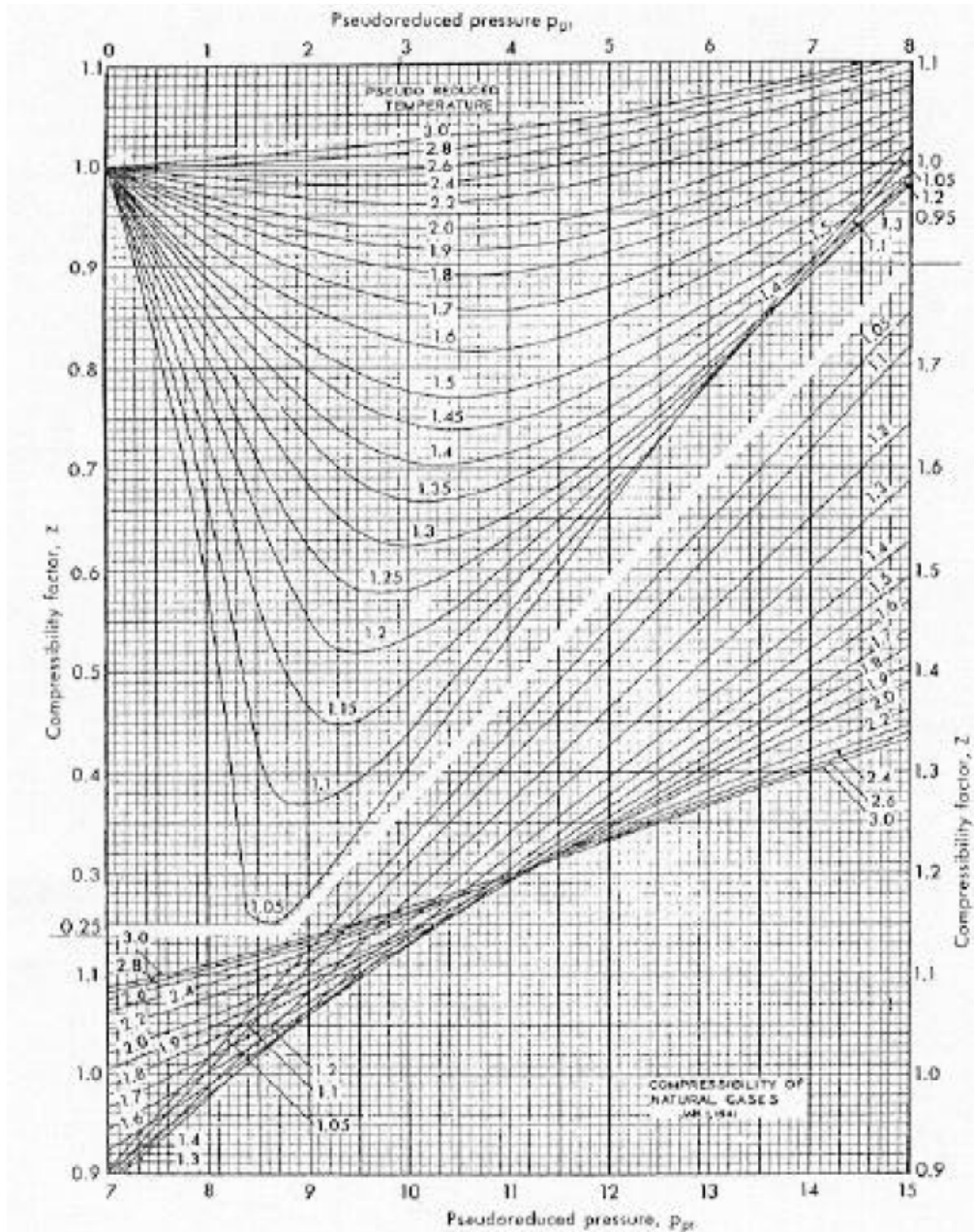


Figure 3 : Compressibility factor of natural gases as a function of reduced pressure and temperature (Standing and Katz, 1942)

Gas Density

Gas density is defined as mass per unit volume and so can also be derived and calculated from the real gas law:

$$\rho_g = \frac{m}{V} = \frac{PM}{ZRT}$$

Knowing that the molecular weight of gas is the product of specific gravity and molecular weight of air and that the value of R is 10.73 in field units [8.314 in SI units], we can write the equation for density as

$$\rho_g = 2.7 \frac{P\gamma_g}{ZI}$$

where ρ_g is in lbm/ft^3 , P is in psia, and T is in $^\circ\text{R}$. Alternately,

$$\rho_g = 3.49 \frac{P\gamma_g}{ZT}$$

Gas Viscosity

Just as the compressibility of natural gas is much higher than that of oil, water, or rock, the viscosity of natural gas is usually several orders of magnitude lower than oil or water. This makes gas much more mobile in the reservoir than either oil or water. Reliable correlation charts are available to estimate gas viscosity, and the viscosity of gas mixtures at one atmosphere and reservoir temperature can be determined from the gas mixture composition:

$$\mu_{ga} = \frac{\sum_{i=1}^N y_i \mu_i \sqrt{M_{gi}}}{\sum_{i=1}^N y_i \sqrt{M_{gi}}}$$

where μ_{ga} is the viscosity of the gas mixture at the desired temperature and atmospheric pressure, y_i is the mole fraction of the i th component, μ_{gi} is the viscosity of the i th component of the gas mixture at the desired temperature and atmospheric pressure, M_{gi} is the molecular weight of the i th component of the gas mixture, and N is the number of components in the gas mixture. This viscosity is then multiplied by the viscosity ratio to obtain the viscosity at reservoir temperature and pressure.

Quality

The amount of energy that is obtained from the burning of a volume of natural gas is measured in British thermal units (Btu). The value of natural gas is calculated by its Btu content.

Transportation

Gas, as a result of the storage difficulties, needs to be transported immediately to its destination after production from a reservoir. There are a number of options for transporting natural gas energy from oil and gas fields to market. These include :

- pipelines,
- liquefied natural gas (LNG),
- compressed natural gas (CNG),
- gas to solids (GTS), i.e., hydrates,
- gas to power (GTP), i.e., electricity,
- gas to liquids (GTL), with a wide range of possible products, including clean fuels, plastic precursors, or methanol

Lecture (4)

BASIC CONCEPTS OF NATURAL GAS PROCESSING

INTRODUCTION

Raw natural gas after transmission through the field-gathering network must be processed before it can be moved into long-distance pipeline systems for use by consumers.

The block flow diagram, figure (4), is a generalized, typical configuration for the processing of raw natural gas from non-associated gas wells. It shows how raw natural gas is processed into sales gas pipelined to the end user markets. It also shows how processing of the raw natural gas yields these byproducts:

- Natural gas condensate
- Sulfur
- Ethane
- Natural gas liquids (NGL): propane, butanes and C_5+ (which is the commonly used term for pentanes plus higher molecular weight hydrocarbons)

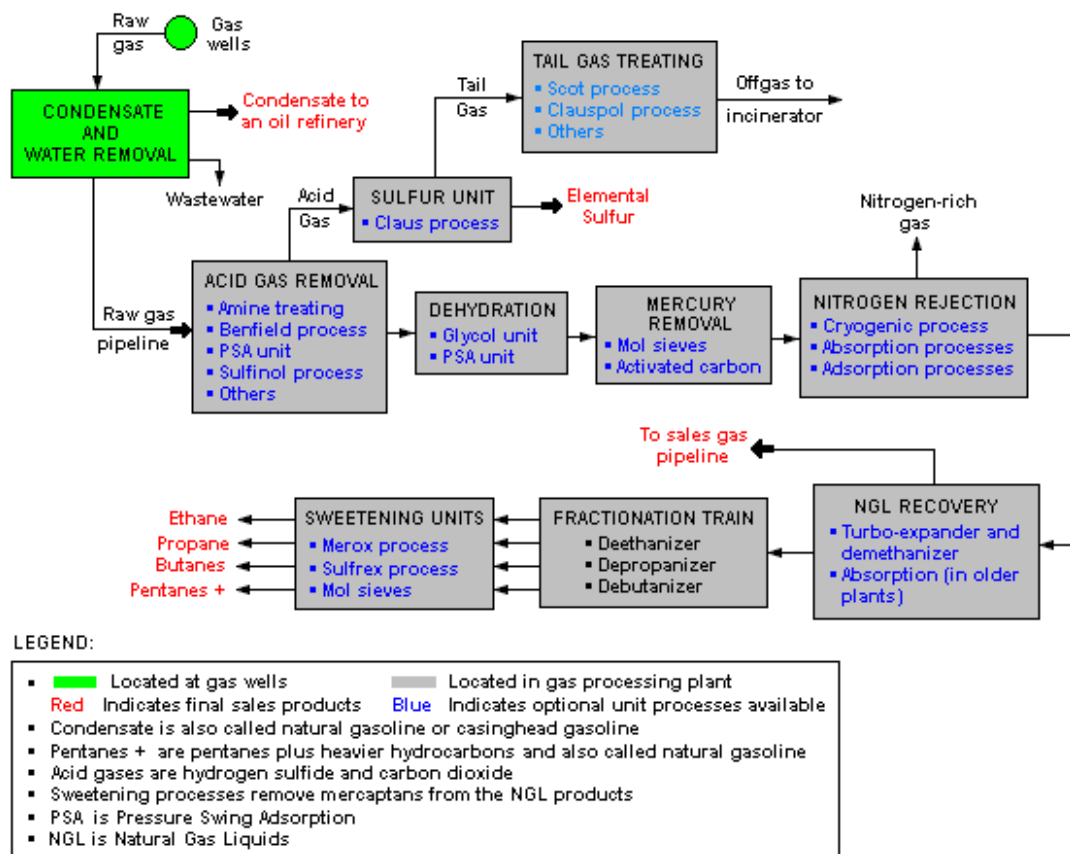


Figure 4: Typical Gas Processing Plant

1. Phase Separation

- Raw natural gas is commonly collected from a group of adjacent wells and is first processed at that collection point for **removal of free liquid water and natural gas condensate**.
- The raw gas is pipelined to a gas processing plant.
- Hydrocarbon condensate recovered from natural gas may be shipped without further processing but is typically stabilized to produce a safe transportable liquid. Unstabilized condensates contain a large percentage of methane and ethane, which will vaporize easily in storage tanks.

Stabilization is the full removal of light fractions from the condensate, usually achieved by distillation. Stabilized liquid will generally have a vapor pressure specification (Reid vapor pressure) of <10 psi, as the product will be injected into a pipeline or transport pressure vessel, which has definite pressure limitations.

2. Acid gas treating (Sweetening).

In addition to heavy hydrocarbons and water vapor, natural gas often contains other contaminants that may have to be removed completely or partially.

- **Carbon dioxide (CO₂),**
- **Hydrogen sulfide (H₂S),**
- **Other sulfur-containing species such as mercaptans**

These compounds are collectively known as **“acid gases.”** H₂S when combined with water forms a weak sulfuric acid, whereas CO₂ and water form carbonic acid, thus the term “acid gas.” **Natural gas with H₂S or other sulfur compounds present is called “sour gas,” whereas gas with only CO₂ is called “sweet.”**

Both H₂S and CO₂ are very undesirable, as they cause corrosion and present a major safety risk.

3. Dehydration

Water dew point control is required to meet specifications and to control hydrate formation. Gas hydrate formation is a major concern for engineers in pipeline and natural gas transportation industries as it causes choking/plugging of pipelines and other related problems.

Methods of preventing hydrate formation in the plant include

- Lowering the hydrate formation temperature with chemical inhibition or
- Dehydration to remove the water.

4. Recovery and Separation of Natural Gas Liquids(NGLs)

- Hydrocarbon dew point or hydrocarbon liquid recovery involves cooling the gas and condensing out the liquids.
- The residue gas from the NGL recovery section is the final, purified sales gas which is pipelined to the end-user markets.
- The recovered NGL stream is processed through a fractionation train consisting of three distillation towers in series: a **deethanizer**, a **depropanizer** and a **debutanizer**.

- The overhead product from the deethanizer is ethane and the bottoms are fed to the depropanizer.
- The overhead product from the depropanizer is propane and the bottoms are fed to the debutanizer.
- The overhead product from the debutanizer is a mixture of normal and iso-butane, and the bottoms product is a C₅+ mixture.
- The recovered streams of propane, butanes and C₅+ are each "*sweetened*" in a ***Merox process*** unit to convert undesirable mercaptans into disulfides and, along with the recovered ethane, are the final NGL by-products from the gas processing plant
- Natural gas specifications in the salable gas stream is given in table (5).

Table 5: Natural Gas Specifications in the Salable Gas

| Characteristic | Specification |
|-----------------------------------|--------------------------|
| Water content | 4–7 lb/MMscf (max) |
| Hydrogen sulfide content | 1/4 grain/100 scf (max) |
| Gross heating value | 950 Btu/scf (min) |
| Hydrocarbon dew point | 15°F at 800 psig (max) |
| Mercaptan content | 0.2 grain/100 scf (max) |
| Total sulfur content | 1–5 grain/100 scf (max) |
| Carbon dioxide content | 1–3 mole percent (max) |
| Oxygen content | 0–0.4 mole percent (max) |
| Sand, dust, gums, and free liquid | Commercially free. |
| Typical delivery temperature | 120°F |
| Typical delivery pressure | 714.7 psia |

Lecture (5)

CONDENSATE STABILIZATION

The process of increasing the amount of intermediates (C_3 to C_5) and heavy (C_6+) components in the condensate is called “*condensate stabilization.*” In other word, the scope of this process is to separate the very light hydrocarbon gases, methane and ethane in particular, from the heavier hydrocarbon components (C_3^+).

STABILIZATION PROCESSES

Stabilization of condensate streams can be accomplished through either *flash vaporization or fractionation.*

1. Flash Vaporization

Stabilization by flash vaporization (Figure 5) is a simple operation employing only two or three flash tanks. This process is similar to stage separation utilizing the equilibrium principles between vapor and condensate phases.

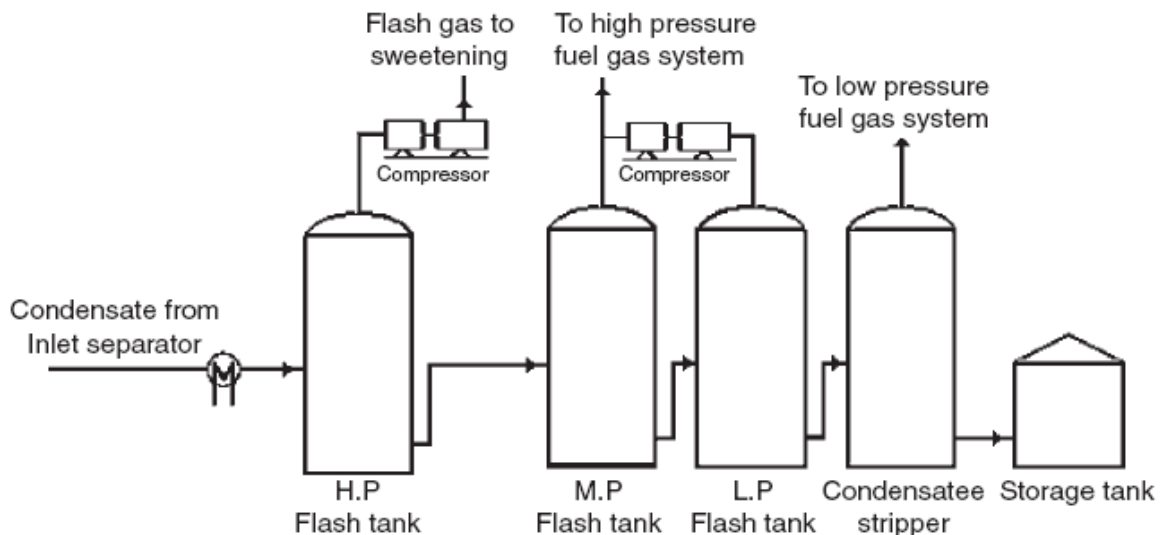


Figure 5: Condensate Stabilization through Flash Vaporization Process
H.P: high pressure; M.P: middle pressure; L.P: low pressure

2. Stabilization by Fractionation

Stabilization by fractionation (Figure 6) is a detailed process, very popular in the industry and precise enough to produce liquids of suitable vapor pressure.

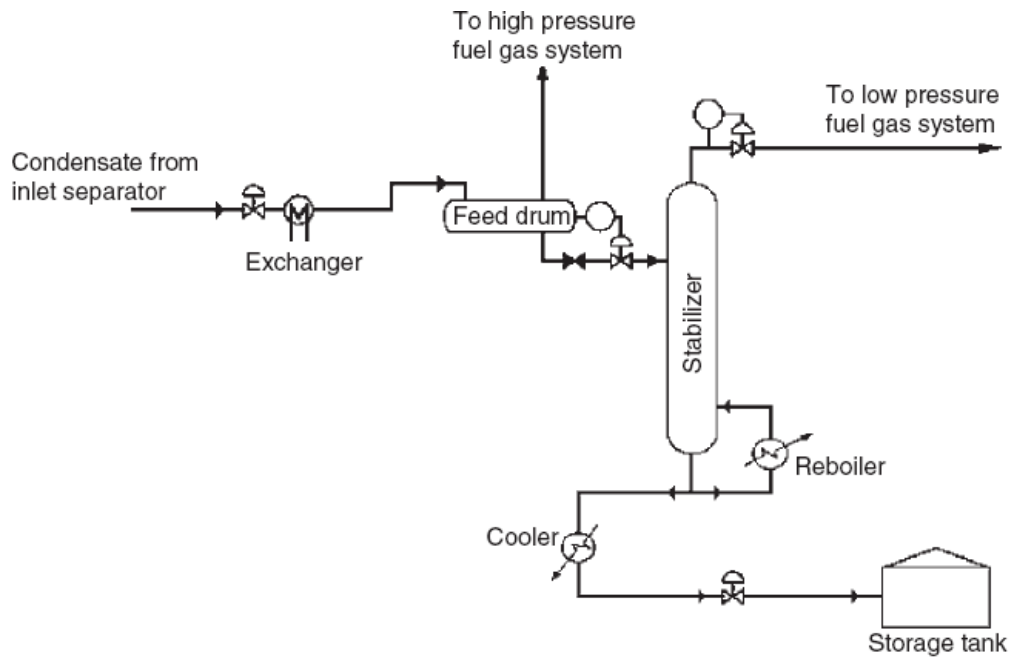


Figure 6: Condensate Stabilization System by Fractionation

In most cases of lease operation, the stabilization column will operate as a nonrefluxed tower. This type of operation is simpler but less efficient than the refluxed tower operation. Because the nonrefluxed tower requires no external cooling source, it is particularly applicable to remote locations.

Lecture (6)

ACID GAS TREATING

Hydrogen sulfide, carbon dioxide, mercaptans, and other contaminants are often found in natural gas streams. Gas sweetening processes remove these contaminants so that the gas is marketable and suitable for transportation. The removal of H₂S from natural gas is accompanied by the removal of CO₂ and COS if present, since these have similar acid characteristics.

Desulfurization processes are primarily of two types:

- adsorption on a solid (dry process), and
- absorption into a liquid (wet process).

Both the adsorption and absorption processes may be of the physical or chemical type. The dominant **sulfur removal/complex train**,

1. amine scrubbing.
2. Claus unit.
3. SCOT-type tail gas treating.

1- Amine Process

Amine gas treating (also known as **Gridler process**) refers to a group of processes that use aqueous solutions of various **amines** to remove **hydrogen sulfide (H₂S)**, **mercaptans** and/or **carbon dioxide (CO₂)** from gases through absorption and chemical reaction.

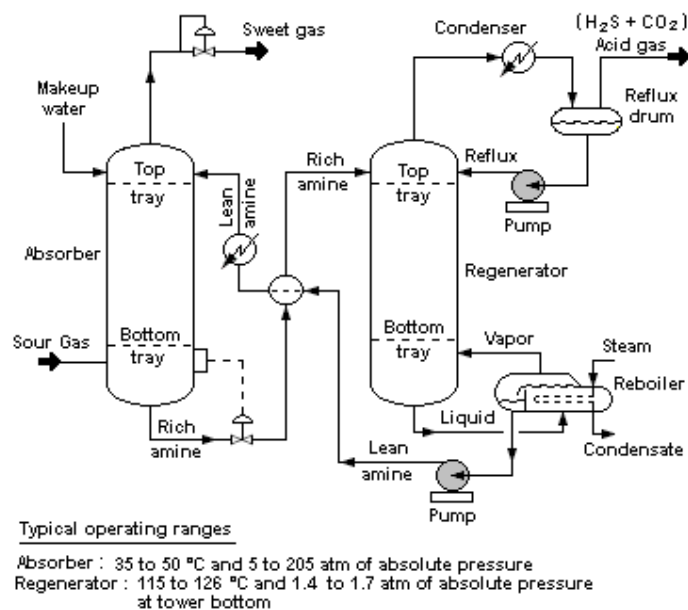


Figure 7: Process flow diagram of a typical amine treating process

The process is also known as **Acid gas removal** and **Gas sweetening** because they results in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide.

A typical amine gas treating process, as shown in figure (7), includes an **absorber** unit and a **regenerator** unit as well as accessory equipments.

2- Sulfinol Process

The **Sulfinol process** is a regenerative process developed to reduce H₂S, CO₂, COS and mercaptans from gases. The sulfur compounds in the product gas can be reduced to low ppm levels. This process has been developed specifically for treating large quantities of gas, such as natural gas, which are available at elevated pressures.

The Sulfinol process is **unique** in the class of absorption processes because it uses a mixture of solvents, which allows it to behave as both a chemical and a physical absorption process.

Features

- Removal of H₂S, COS and organic sulfur to natural gas pipeline specification.
- Low steam consumption and solvent circulation.
- Low corrosion rate.
- Selective removal of H₂S in some natural gas applications.
- Smaller equipment due to low foaming tendency.

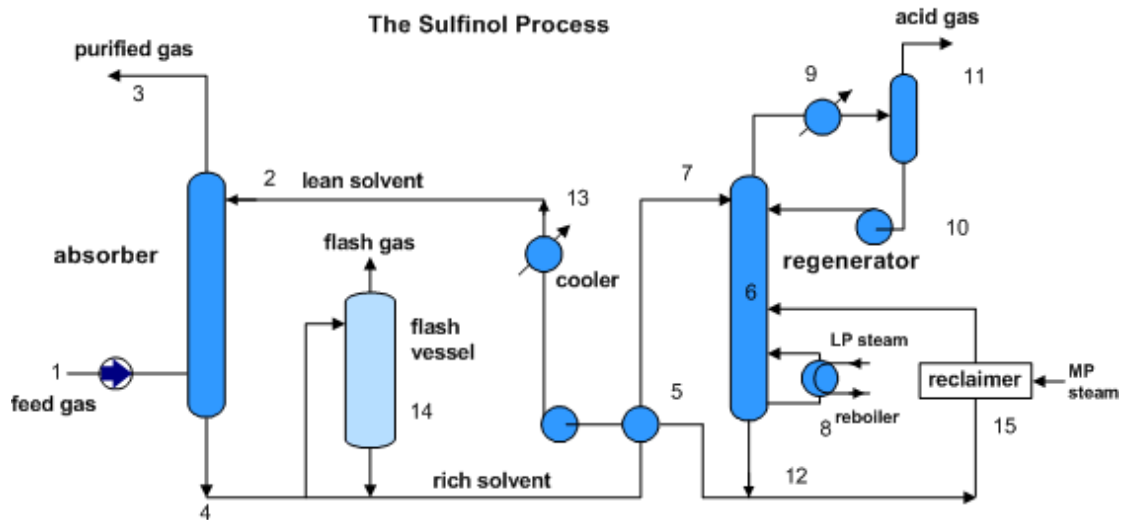


Figure 8: Sulfinol Process

3- Claus Sulfur Recovery Processes

Hydrogen sulfide (H₂S) is a smelly, corrosive, highly toxic gas. It also deactivates industrial catalysts. H₂S is commonly found in natural gas and is also made at oil refineries, especially if the crude oil contains a lot of sulfur compounds.

Because H₂S is such an obnoxious substance, it is converted to non-toxic and useful elemental sulfur at most locations that produce it. The process of choice is the **Claus Sulfur Recovery process**.



Description of the Claus Process

First the H_2S is separated from the host gas stream using *amine absorption*. Then it is fed to the Claus unit, where it is converted in two steps as shown in figure (9).

1. **Thermal Step.** The H_2S is partially oxidized with air. This is done in a reaction furnace at high temperatures (1000-1400 deg C). Sulfur is formed, but some H_2S remains unreacted, and some SO_2 is made.



Catalytic Step. The remaining H_2S is reacted with the SO_2 at lower temperatures 450 deg F (about 200-350 deg C) > dew point of S to prevent condensation on the catalyst, to make more sulfur. A catalyst is needed in the second step to help the components react with reasonable speed. Unfortunately the reaction does not go to completion even with the best catalyst. For this reason two or three stages are used, with sulfur being removed between the stages. Engineers know how different factors like concentration, contact time and reaction temperature influence the reaction, and these are set to give the best conversions.



Condenser outlet must be $350^\circ F$ > melting point of S to prevent the formation of solid S. Inevitably a small amount of H_2S remains in the tail gas. This residual quantity, together with other trace sulfur compounds, COS and CS_2 , formed in the burner side reaction, is usually dealt with in a *tail gas unit*. The latter can give overall sulfur recoveries of about 99.8%.

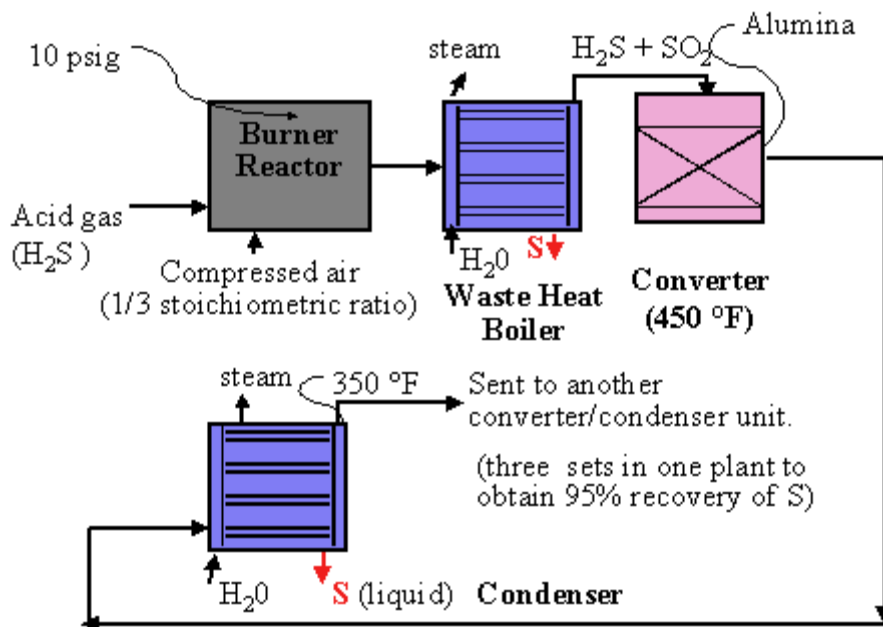


Figure 9: Claus Process

4- The SCOT Process

Because of the more stringent requirements of pollution control, requirements for tail gas clean-up processes are developed. **The SCOT** process is an example.

In the first stage, the Claus tail gas is heated to about 570 0F and reacted with H₂ over a cobalt molybdenum catalyst. All the COS, CS₂, S and SO₂ in the Claus unit off gas are converted to H₂S (Fig.10) by the following reaction



These reactions are highly exothermic. The hot gas from the reactor is cooled in a waste heat boiler and finally quenched in a water cooling tower. The final stage involves the selective absorption of H₂S in an amine solution, normally DIPA. The vent gas from the SCOT absorber typically contains 200–500 ppmv of H₂S. This vent is normally incinerated before discharging to the atmosphere. The rich amine is stripped in a conventional manner, and the H₂S rich stream is recycled back to the front of the Claus plant.

The Claus + SCOT processes combine to remove 99.5% of the S

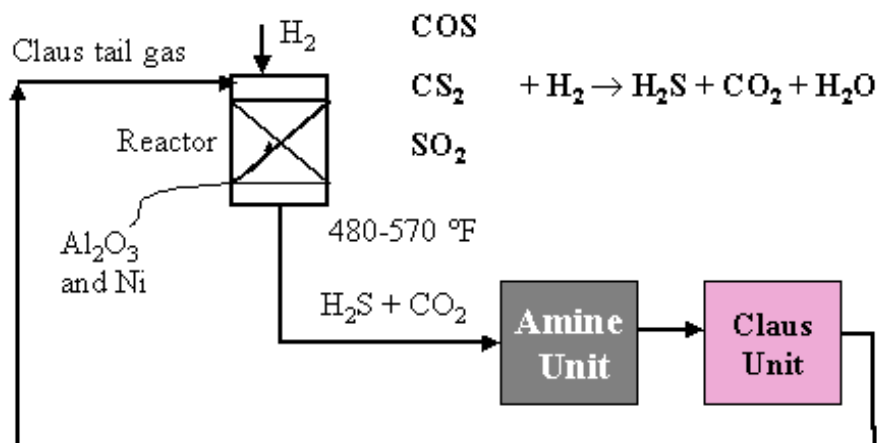


Figure 10: The SCOT Process

Lecture (7)

GAS DEHYDRATION

Introduction

Natural gas dehydration is the process of *removing water vapor from the gas stream to lower the dew point of that gas*. The dew point is defined as the temperature at which water vapor condenses from the gas stream. The sale contracts of natural gas specify either its dew point or the maximum amount of water vapor present.

There are three basic reasons for the dehydration of natural gas streams:

1. To prevent hydrate formation.
2. To avoid corrosion problems.
3. Downstream processing requirements.

Water Content of Hydrocarbons

In any mixture, where both the gas and liquid phases are in equilibrium, each component, i , in the mixture obeys the relationship

$$x_i \gamma_i P_i^{Sat} = y_i \phi_i P$$

However, reasonably good estimates of the concentration of water in the vapor phase in equilibrium with liquid water can be made at pressures below 500 psia (35 bar). If we make the good assumption of negligible hydrocarbon in the liquid water phase, which, thus makes both x_i and ϕ_i unity for water and assume the gas phase to be ideal, which makes j_i unity, we obtain

$$y_{H_2O} = \frac{P_{H_2O}^{Sat}}{P}$$

Example: Calculate the water content of the given sweet natural gas at 300 psia (20.7 bar) and 80°F (26.7°C)

| Component | Mole Fraction |
|----------------------------------|---------------|
| CH ₄ | 0.90 |
| C ₂ H ₆ | 0.04 |
| C ₃ H ₈ | 0.03 |
| n-C ₄ H ₁₀ | 0.02 |
| N ₂ | 0.01 |
| Totals | 1.00 |

Dehydration Methods

Two processes, absorption and adsorption, are the most common for drying natural gas

- **Absorption (Glycol Dehydration Process)**

In this process (Fig. 11), a hygroscopic liquid is used to contact the wet gas to remove water vapor from it. Triethylene glycol (TEG) is the most common solvent used.

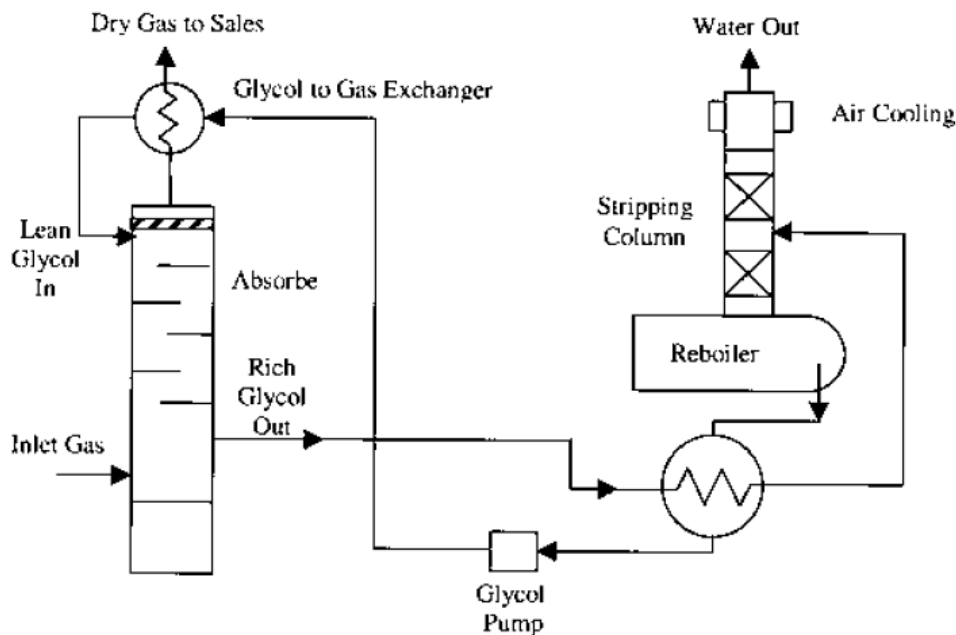


Figure 11: Flow Diagram of TEG Dehydration

- **Adsorption: Solid-Bed Dehydration**

- ✚ Solid desiccant dehydration systems work on the principle of adsorption.
- ✚ Adsorption involves a form of adhesion between the surface of the solid desiccant and the water vapor in the gas.
- ✚ The water forms an extremely thin film that is held to the desiccant surface by forces of attraction, but there is no chemical reaction.
- ✚ Solid desiccant dehydrators are typically more effective than glycol dehydrators, as they can dry a gas to less than 0.1 ppmV (0.05 lb/MMcf).
- ✚ However, in order to reduce the size of the solid desiccant dehydrator, a glycol dehydration unit is often used for bulk water removal. The glycol *Natural Gas* unit would reduce the water content to around 60 ppmV, which would help reduce the mass of solid desiccant necessary for final drying.
- ✚ Using desiccant dehydrators as alternatives to glycol dehydrators can yield significant economic and environmental benefits, including reduced capital cost, reduced operation and maintenance cost, and minimal VOC and hazardous air pollutants (BTEX).

Three types of commercial adsorbents are in common use in gas processing plants:

- Silica gel, which is made of pure SiO_2
- Activated alumina, which is made of Al_2O_3

- Molecular sieves, which are made of alkali aluminosilicates and can be altered to affect adsorption characteristics.

Silica gels: Are used mostly where a high concentration of water (>1 mol%) vapor is present in the feed, and low levels of water in the dehydrated gas are not needed. They are relatively noncatalytic compounds.

Aluminas: Are very polar and strongly attract water and acid gases. They are used for moderate levels of water in the feed when low levels of water in the product are not required. They have the highest mechanical strength of the adsorbents considered here.

Molecular sieves: For gas going into cryogenic processing, the only adsorbent that can obtain the required dehydration is a molecular sieve.

The system as shown in Figure 12 may consist of two-bed, three-bed, or Multi-bed operation. In the three-bed operation, if two beds are loading at different stages, the third one would be regenerated. The operation of the process is controlled by opening valve (↑) and closing valve (↓). After the bed has been used and loaded with water, then it is regenerated by hot gas (say 6 h, as heating time) and then cooled by switching to cold gas (say for 2 h).

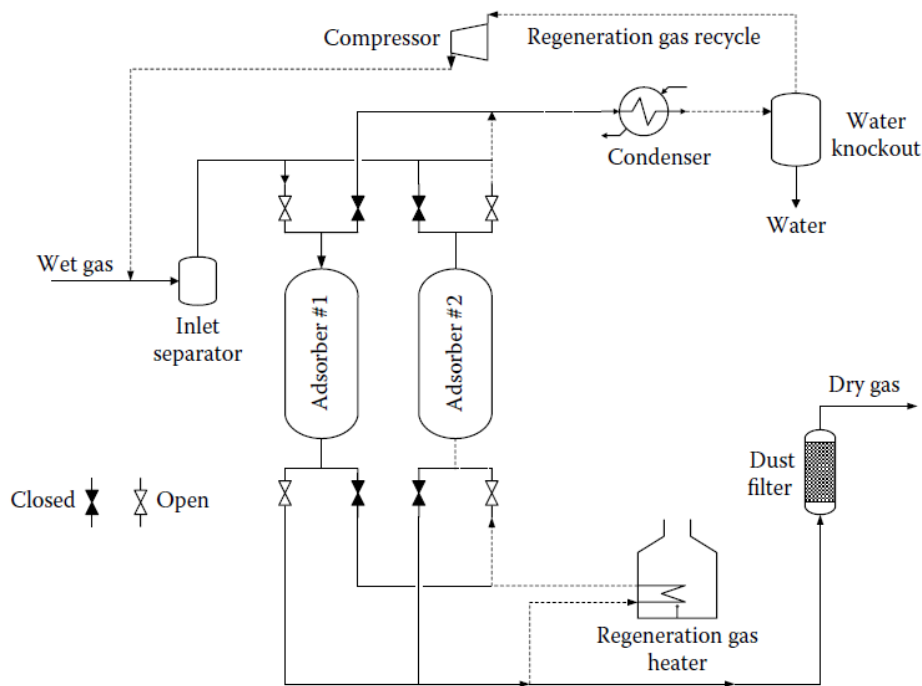


Figure 12: Solid-Bed Dehydration Process

Lecture (8)

RECOVERY, SEPARATION, AND FRACTIONATION OF NATURAL GAS LIQUIDS

Introduction:

Natural gas coming directly from a well contains many natural gas liquids that are commonly removed. In most instances, natural gas liquids (NGLs) have a higher value as separate products, and it is thus economical to remove them from the gas stream. The removal of natural gas liquids usually takes place in a relatively centralized processing plant, and uses techniques similar to those used to dehydrate natural gas.

There are two basic steps to the treatment of natural gas liquids in the natural gas stream. First, the liquids must be extracted from the natural gas. Second, these natural gas liquids must be separated themselves, down to their base components.

To recover and separate NGL from a bulk of gas stream, a change in phase has to take place. In other words, a new phase has to be developed for separation to occur. Two distinctive options are in practice depending on the use of

- **Energy Separating Agent (ESA) or**
- **Mass Separating Agent (MSA).**

Energy Separating Agent

The distillation process best illustrates a change in phase using ESA. To separate, for example, a mixture of alcohol and water heat is applied. A vapor phase is formed in which alcohol is more concentrated, and then separated by condensation. This case of separation is expressed as follows:

A mixture of liquids + Heat \rightarrow Liquid + Vapor

For the case of NGL separation and recovery in a gas plant, removing heat (by refrigeration) on the other hand, will allow heavier components to condense; hence, a liquid phase is formed. This case is represented as follows:

A mixture of hydrocarbon vapor – Heat \rightarrow Liquid + Vapor

Partial liquefaction is carried out for a specific cut, whereas total liquefaction is done for the whole gas stream.

Mass Separating Agent

To separate NGL, a new phase is developed by using either a solid material in contact with the gas stream (adsorption) or a liquid in contact with the gas (absorption).

LIQUIDS CONTENT

Gas composition plays a critical role in the economics of gas processing. The more liquids, usually defined as C_2^+ , in the gas, the “richer” the gas. Extraction of these liquids produces a product that may have a higher sales value than does natural gas.

To quantify the liquids content of a natural gas mixture, the industry uses GPM, or gallons of liquids recoverable per 1,000 standard cubic feet (Mscf) of gas. (In metric units, the quantity is commonly stated as m^3 of liquid per 100 m^3 of gas.) The term usually applies to ethane and heavier components but sometimes applies instead to propane and heavier components. Determination of the GPM requires knowledge of the gas composition on a mole basis and

the gallons of higher hydrocarbons. Note that ethane is not a liquid at 60°F (15.5°C), so the value is a hypothetical value accepted throughout the industry.

Parameters Controlling NGL Separation

A change in phase for NGL recovery and separation always involves control of one or more of the following three parameters:

- Operating pressure, P
- Operating temperature, T
- System composition or concentration, x and y

To obtain the right quantities of specific NGL constituents, a control of the relevant parameters has to be carried out:

1. For separation using ESA, pressure is maintained by direct control. Temperature, on the other hand, is reduced by refrigeration using one of the following techniques:

- (a) Compression refrigeration
- (b) Cryogenic separation; expansion across a turbine
- (c) Cryogenic separation; expansion across a valve

2. For separation using MSA, a control in the composition or the concentration of the hydrocarbons to be recovered (NGL); y and x is obtained by using adsorption or absorption methods.

The *efficiency* of condensation, hence NGL recovery, is a function of **P, T, gas and oil flow rates, and contact time**. Again, absorption could be coupled with refrigeration to enhance condensation.

Absorption Process

The absorption unit, Fig. 13, consists of two sections:

- Absorption
- Regeneration
- An upflow natural gas stream is brought in direct contact, countercurrently with the solvent (light oil in the kerosene boiling range) in the absorber.
- The column—a tray or packed one—operates at about 400–1000 psia and ambient or moderately subambient temperatures.
- The rich oil (absorbed NGL plus solvent) is directed to a distillation unit to separate and recover the NGL, whereas the lean oil is recycled back to the absorber.
- In addition to natural gasoline, C₃/C₄ could be recovered as well in this process.
- Provision is made to separate ethane from rich oil using a deethanizer column. Ethane recovery, however, is quite small. This process is being phased out.
- This process allows for the recovery of around 75 percent of butanes, and 85 - 90 percent of pentanes and heavier molecules from the natural gas stream.

The basic absorption process above can be *modified* to improve its effectiveness, or to target the extraction of specific NGLs. In the refrigerated oil absorption method, where the lean oil is cooled through refrigeration, propane recovery can be upwards of 90 percent, and around

40 percent of ethane can be extracted from the natural gas stream. Extraction of the other, heavier NGLs can be close to 100 percent using this process.

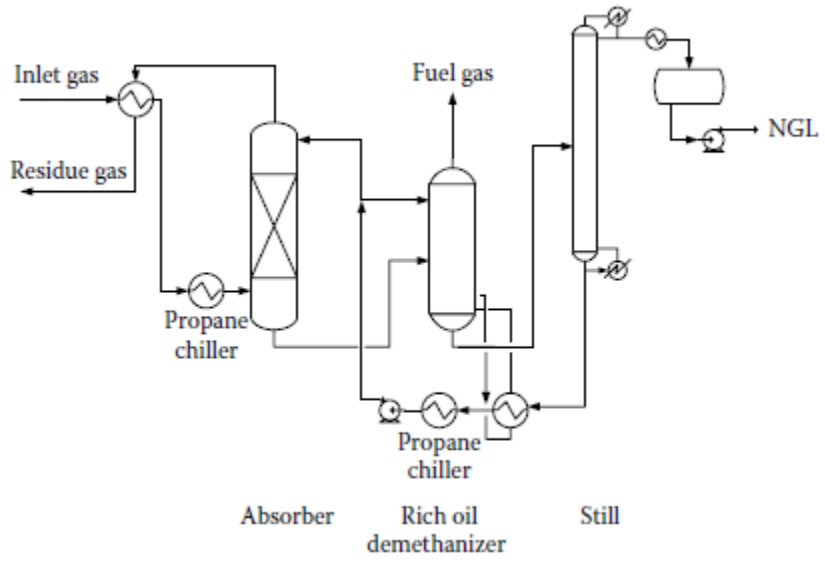


Figure 13: Refrigerated Lean Oil Absorption Process

Refrigeration Process

The production of NGL at low temperature is practiced in many gas processing plants in order to condense NGL from gas streams. As indicated in Figure 14, using *nontoxic and noncorrosive refrigerants* to chill the feed natural gas to a temperature between **0°F and -40°F** using a low level one-component refrigerant system provides external refrigeration. When using a high-level cascade refrigerant system, a much lower temperature in the range of -100°F to -150°F is reached. Liquids are separated from the residue gas at multiple temperatures and then fractionated into final products. Ethane recovery is a strong function of the operating temperatures as is explained next.

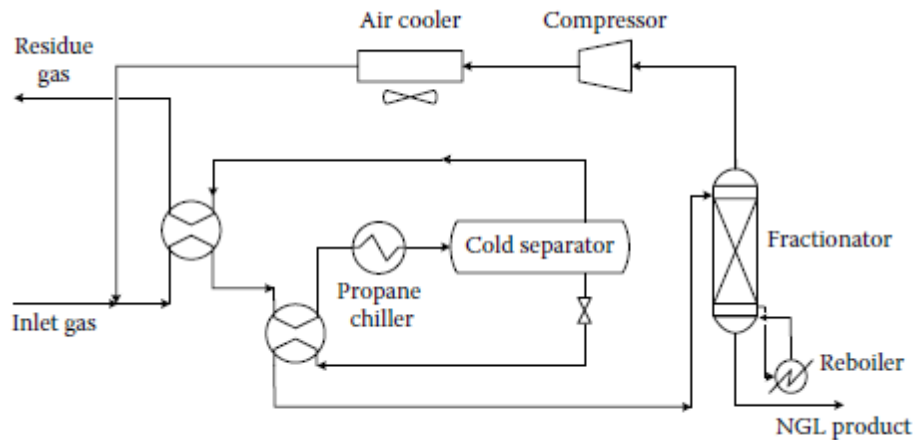


Figure 14: Schematic of Direct Refrigeration Process for Partial Recovery of C₂⁺ Fraction

The schematic flow diagram above shows one commonly used direct-refrigeration process that employs recycle from a fractionator to maximize liquids recovery. Inlet gas is initially cooled with cold residue gas and cold liquid from the cold separator before going to the propane chiller and to the cold separator. Vapor from the separator is the sales gas, and the liquid goes to a fractionator to strip out light ends and recover liquid product.

The column operates at a lower pressure than does the cold separator. Because of system pressure drop and because the fractionator runs at the lower pressure, the recycle stream must be recompressed.

Cryogenic Processes

Natural gas liquid could be separated from natural gas using two approaches based on cryogenic expansion (autorefrigeration):

- An expander plant (Fig.15) produces refrigeration to condense and recover the liquid hydrocarbons contained in the natural gas by using a turboexpander. In this process, the enthalpy of the natural gas is converted into useful work, behaving thermodynamically as an approximate isentropic process.
- Expansion across the valve (Fig.16) will lead to a similar result. However, the expansion is described in this case as “isenthalpic.”

Temperatures produced by turboexpansion are much lower than those of valve expansion. The turbo expander process operates at -100 °F to -160 °F and 1000 psia. The process represents a new development in the gas processing industry. Increased liquid recovery (especially ethane) is an advantage of this process.

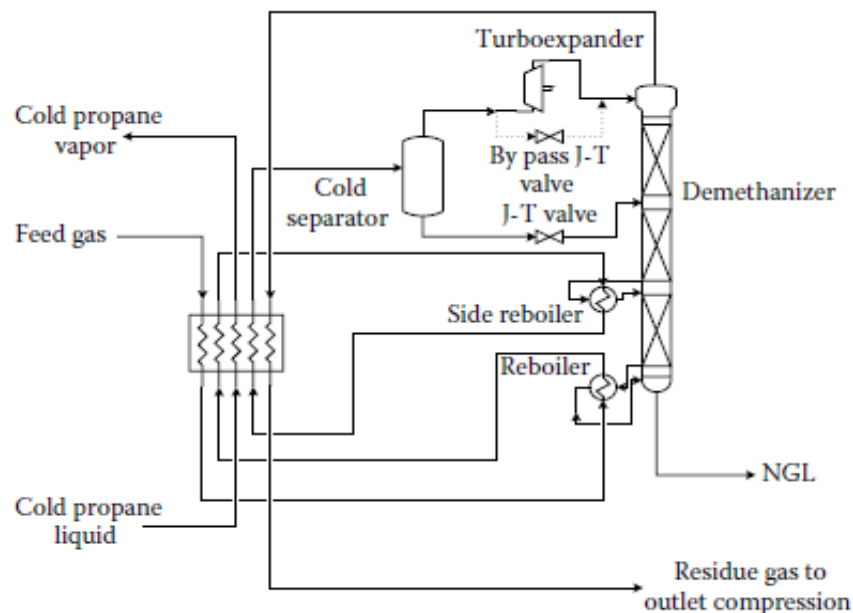


Figure 15: Schematic of Cryogenic Separation, Expansion across Turbine

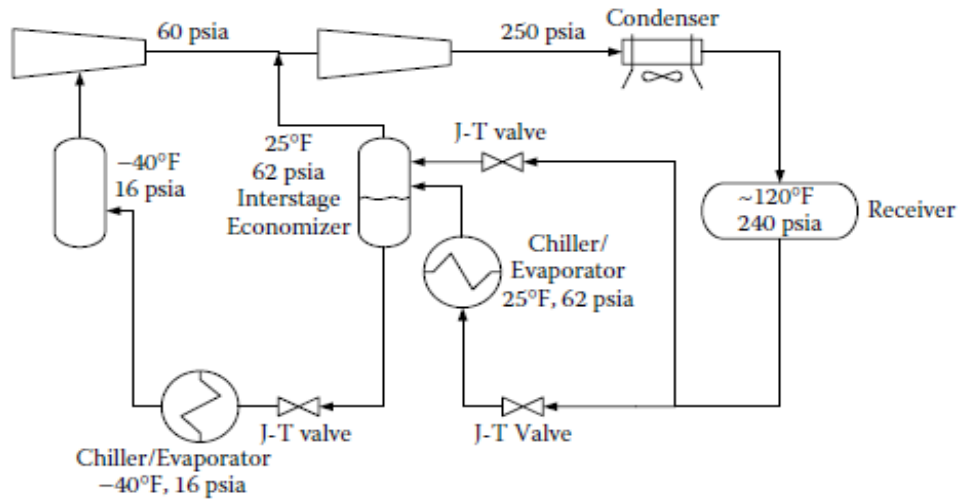


Figure 16: Schematic of a Cryogenic Separation, Expansion across Valve