

University of Technology
Chemical Eng. Department



Gas Technology Lectures
4th Year/Petroleum Refinery Engineering Branch
By
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CE 744-R

Gas Technology

Units 2
 Theoretical 2 hr/week
 Tutorial 1 hr/week
 Practical - hr/week

Refinery Engineering Branch

1. Classification of Gaseous fuels thermodynamic: (3 hrs)
2. Physical and Chemical Properties for natural Gas: (3 hrs)
3. Drying of Gaseous Fuels:
 Drying by Adsorption, Drying by Absorption (4 hrs)
4. Sweetening of Gaseous Fuels:
 Sweetening by Adsorption, Sweetening by Absorption (6 hrs)
5. Gas Processing units:
 Flash Separation Processes, Distillation of multicomponent gas mixture (6 hrs)
6. Liquefied Petroleum Gases: (2 hrs)
7. Production of Hydrogen: (2 hrs)
8. Sulfur recovery processes from Acid gases streams: (4 hrs)

NATURAL GAS FUNDAMENTALS

Origin & World Reserves

Natural gas is generally considered a ***nonrenewable fossil fuel***. Natural gas is called a fossil fuel because most scientists believe that natural gas was formed from the remains of tiny sea animals and plants that died 200-400 million years ago.

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

Raw natural gas comes primarily from any one of three types of gas wells.

- 1) crude oil wells
- 2) gas wells
- 3) condensate wells.

Natural gas wells average ***6000 feet deep***.

Natural gas produced from geological formations comes in a wide array of compositions. The varieties of gas compositions can be broadly categorized into three distinct groups:

- (1) ***Nonassociated*** gas that occurs in conventional gas fields,
- (2) ***Associated gas*** that occurs in conventional oil fields,
- (3) ***Continuous (or unconventional) gas***. Some types of unconventional gas resources include

“tight gas”

“coalbed methane

“natural gas from geopressurized aquifers,”

“gas hydrates,”

“deep gas,”

Of the unconventional gas sources, the one most important to the gas transportation industry is ***coal bed methane***. Figure (1) shows the world natural gas reserves.

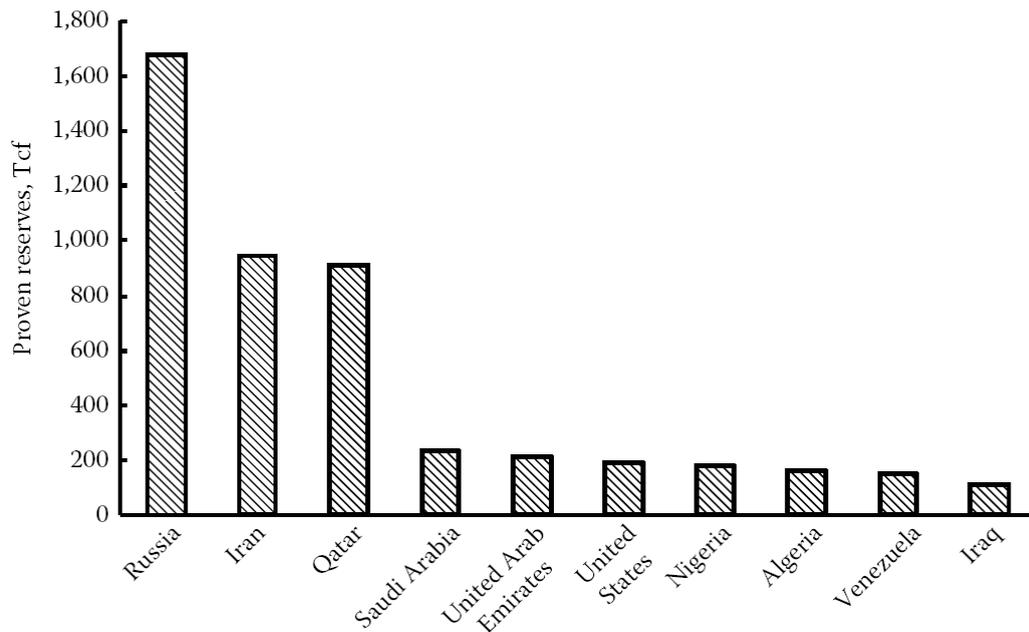


Fig. (1); World Natural Gas Reserves – 2006

Natural gas is used primarily as a *fuel and as a raw material in manufacturing*, Fig. (2).

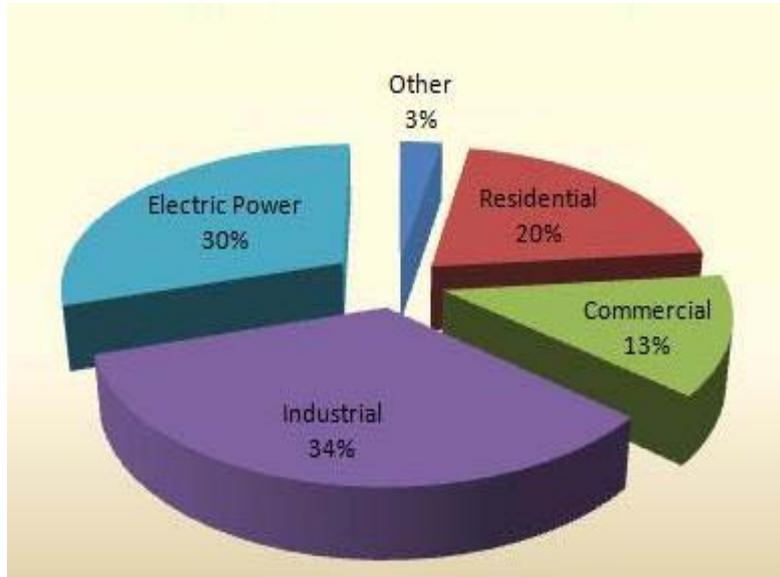


Fig. (2): Natural Gas Uses - 2007

Natural gas can be used in;

- ✚ Power generation
- ✚ Hydrogen production
- ✚ Vehicles
- ✚ Residential domestic use



Fertilizer

Aviation

Natural gas is also used in the manufacture of fabrics, glass, steel, plastics, paint, and other products.

Composition

Natural gas is a complex mixture of hydrocarbon and non-hydrocarbon constituents and exists as a gas under atmospheric conditions.

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 ($n-C_4H_{10}$), iso-butane ($i-C_4H_{10}$), 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 (C_2H_5SH).
- 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.

Table (1) outlines the typical makeup of natural gas before it is refined. 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.

Name	Formula	Volume (%)
Methane	CH ₄	>85
Ethane	C ₂ H ₆	3–8
Propane	C ₃ H ₈	1–2
Butane	C ₄ H ₁₀	<1
Pentane	C ₅ H ₁₂	<1
Carbon dioxide	CO ₂	1–2
Hydrogen sulfide	H ₂ S	<1
Nitrogen	N ₂	1–5
Helium	He	<0.5

Table 1: Typical Composition of Natural Gas

Gas Specifications

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.

Irrespective of the source of natural gas, the final specifications set for market sales requirements are usually the following:

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

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:

Water vapor	H ₂ S and CO ₂	Liquid hydrocarbons
<p>It is a common impurity. It is not objectionable as such.</p> <p>(a) Liquid water accelerates corrosion in the presence of H₂S gas.</p> <p>(b) Solid hydrates, made up of water and hydrocarbons, plug valves, fittings in pipelines, and so forth.</p>	<p>Both gases are harmful, especially H₂S, which is toxic if burned; it gives SO₂ and SO₃ which are nuisance to consumers.</p> <ul style="list-style-type: none"> Both gases are corrosive in the presence of water. CO₂ contributes a lower heating value to the gas. 	<p>Their presence is undesirable in the gas used as a fuel.</p> <ul style="list-style-type: none"> The liquid form is objectionable for burners designed for gas fuels. 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 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. The phase behavior for natural gas with a given composition is typically displayed on a phase diagram, an example of which is shown in Figure (3).

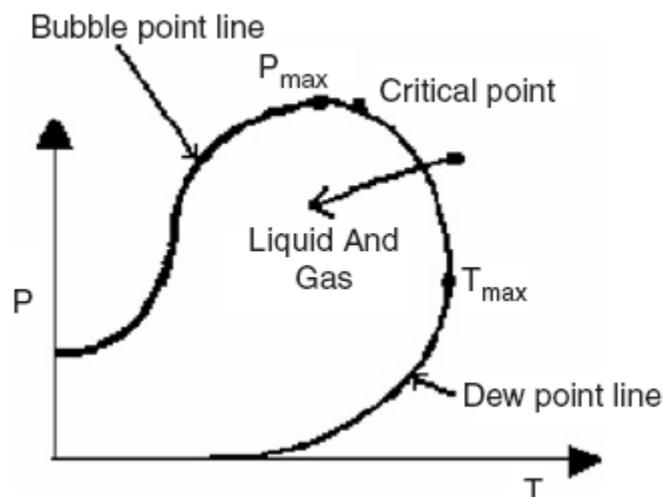


Fig.(3): Pressure-temperature diagram for a typical natural gas mixture.

Natural Gas Properties

- *Chemical and Physical Properties*

Natural gas is colorless, odorless, tasteless, shapeless, and lighter than air (Table 1). 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*).

Table(1): 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

1. 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

$$M = \sum_{i=1}^n y_i M_i \text{-----(2)}$$

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.

Various gas properties, including the molecular weights for pure components, are given in Table 2.

2. Ideal and Real Gas Laws

The volume of a real gas is usually less than what the volume of an ideal gas would be, and hence a real gas is said to be supercompressible. The ratio of the real volume to the ideal volume, which is a measure of the amount the gas deviates from perfect behavior, is called the supercompressibility factor, sometimes shortened to the compressibility factor. It is also called the gas deviation factor and is given the symbol Z . The real gas equation of state is then written as:

$$PV = ZnRT \text{-----(3)}$$

where P is the pressure, V is the volume, T is the absolute temperature, Z is the compressibility, n is the number of kilomoles of the gas, and R is the gas constant.

The theory of corresponding states dictates that the Z factor can be uniquely defined as a function of reduced pressure and reduced temperature. The reduced pressure and reduced temperature are defined as

$$P_r = \frac{P}{P_c} \text{ and } T_r = \frac{T}{T_c} \text{-----(4)}$$

Table 2

Physical Constants for Pure Components (Whitson and Brule, 2000)

Compound	Formula	Molecular weight	Critical constants			
			P_c psia [kPa]	T_c °K [°K]	V_c ft ³ /lb [m ³ /kg]	Z_c
Methane	CH ₄	16.043	667.8[4,604]	343[190.6]	0.0991[0.0062]	0.28884
Ethane	C ₂ H ₆	30.070	707.8[4,880]	549.8[369.8]	0.0788[0.00492]	0.2843
Propane	C ₃ H ₈	44.097	6163[4,249]	665.7[369.8]	0.0737[0.0046]	0.2804
<i>n</i> -Butane	C ₄ H ₁₀	58.124	550.7[3,797]	765.3[425.2]	0.702[0.00438]	0.2736
Isobutane	C ₄ H ₁₀	58.124	529.1[3,648]	734.7[408.2]	0.0724[0.00452]	0.2824
<i>n</i> -Pentane	C ₅ H ₁₂	72.151	488.6[3,369]	845.4[469.7]	0.0675[0.00422]	0.2623
Isopentane	C ₅ H ₁₂	72.151	490.4[3,381]	828.8[460.4]	0.0679[0.00424]	0.2701
Neopentane	C ₅ H ₁₂	72.151	464.0[3,199]	781.11	0.0674[0.00421]	0.2537
<i>n</i> -Hexane	C ₆ H ₁₄	86.178	436.9[3,012]	913.4[507.4]	0.0688[0.0043]	0.2643
<i>n</i> -Heptane	C ₇ H ₁₆	100.205	396.8[2,736]	972.5[5403]	0.0691[0.00432]	0.2633
<i>n</i> -Octane	C ₈ H ₁₈	114.232	360.6[2,486]	1,023.9[568.8]	0.0690[0.0043]	0.2587
<i>n</i> -Nonane	C ₉ H ₂₀	128.30	332[2,289]	1,0703[594.6]	0.0684[0.00427]	0.2536
<i>n</i> -Decane	C ₁₀ H ₂₂	142.30	304.[2,096]	1,111.8[617.7]	0.0679[0.00424]	0.2462
Ethylene	C ₂ H ₄	28.054	729.8[5,032]	508.6[282.6]	0.0737[0.0046]	0.2765
Propene	C ₃ H ₆	42.081	699.[4,613]	6569[364.9]	0.0689[0.0043]	0.2752
Acetylene	C ₂ H ₂	26.038	890.4[6,139]	555.3[308.5]	0.0695[0.00434]	0.2704
Carbon dioxide	CO ₂	44.010	1071.[7,382]	547.6[304.2]	0.0342[0.00214]	0.2742
Hydrogen sulfide	H ₂ S	34.076	1306[9,005]	672.4[373.6]	0.0459[0.00287]	0.2831
Sulfur dioxide	SO ₂	64.059	1145.[7,894]	775.5[430.8]	0.0306[0.00191]	0.2697
Nitrogen	N ₂	28.013	493[3,399]	227.3[126.3]	0.0514[0.00321]	0.2916
Water	H ₂ O	18.015	3208.[22,105]	1,1650[647.2]	0.0500[0.00312]	0.2350

where P_r and T_r are reduced pressure and reduced temperature, respectively, and P_c and T_c are critical pressure and critical temperature of the gas, respectively. The values of critical pressure and critical temperature can be estimated from the following equations if the composition of the gas and the critical properties of the individual components are known:

$$P_c = \sum_i^n P_{ci}y_i \text{ and } T_c = \sum_i^n T_{ci}y_i \text{-----(5)}$$

where P_{ci} and T_{ci} are the critical pressure and critical temperature of component i , respectively; and y_i is the mole fraction of component i . The values of critical pressure and critical temperature can be estimated from its specific gravity if the composition of the gas and the critical properties of the individual components are not known. Sutton (1985) used regression analysis on raw data to obtain the following second-order fits for the pseudocritical properties:

$$P_{pc} = 756.8 - 131.07\gamma_g - 3.6\gamma_g^2$$

$$T_{pc} = 169.2 + 349.5\gamma_g - 74.0\gamma_g^2$$

These equations are valid over the range of specific gas gravities with which Sutton (1985) worked $0.57 < \gamma_g < 1.68$.

The most commonly used method to estimate the Z factor is the chart provided by Standing and Katz (1942). The Z factor chart is shown in Fig.(4).

3. Gas Formation Volume Factor

The formation volume factor for gas is defined as the ratio of volume of 1 mol of gas at a given pressure and temperature to the volume of 1 mole of gas at standard conditions (P_s and T_s). Using the real gas law and assuming that the Z factor at standard conditions is 1, the equation for formation volume factor (B_g) can be written as

$$B_g = \frac{V_R}{V_s} = \frac{nZRT}{P} \frac{P_s}{nZ_sRT_s} = \frac{P_s Z T}{T_s P}$$

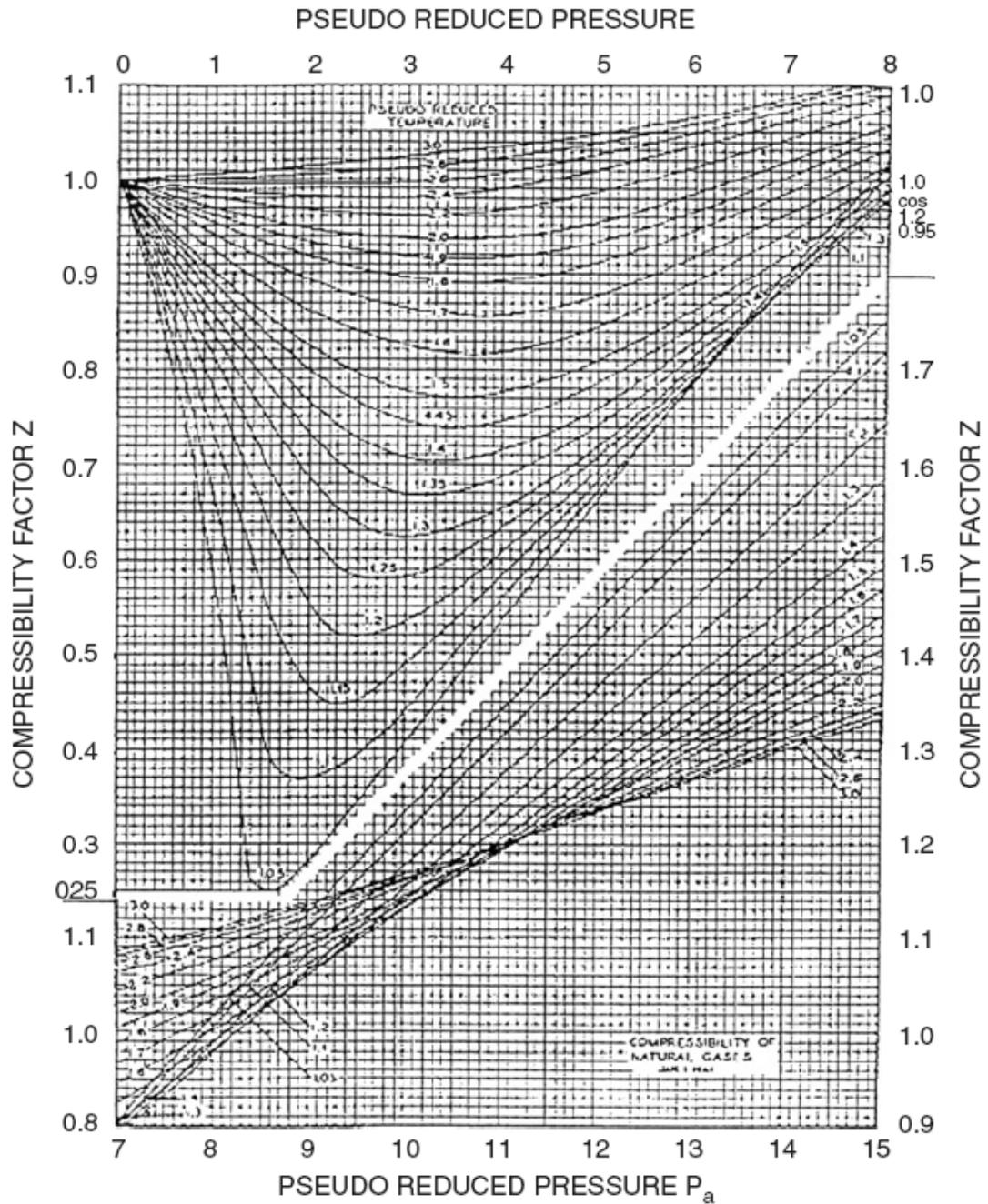


Fig. (4): Compressibility of natural gases as a function of reduced pressure and temperature (Standing and Katz, 1942).

4. Gas Density

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

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

5. Isothermal Compressibility of Gases

The isothermal gas compressibility, which is given the symbol c_g , is a useful concept is used extensively in determining the compressible properties of the reservoir. The isothermal compressibility is also called the bulk modulus of elasticity. Gas usually is the most compressible medium in the reservoir. However, care should be taken so that it is not confused with the gas deviation factor, Z , which is sometimes called the supercompressibility factor:

$$c_g = -\frac{1}{V_g} \left(\frac{\partial V_g}{\partial P} \right)_T$$

where V and P are volume and pressure, respectively, and T is the absolute temperature. For ideal gas, we can define the compressibility as

$$c_g = \frac{1}{P}$$

whereas, for nonideal gas, compressibility is defined as

$$c_g = \frac{1}{P} - \frac{1}{Z} \left(\frac{\partial Z}{\partial P} \right)_T$$

6. 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_i 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.

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 objective of gas processing is to separate

- natural gas,
- condensate,
- noncondensable,
- acid gases, and
- water

from a gas-producing well and condition these fluids for sale or disposal. The typical process operation modules are shown in Figure 1. Each module consists of a single piece or a group of equipment performing a specific function. All the modules shown will not necessarily be present in every gas plant. In some cases, little processing is needed; however, most natural gas requires processing equipment at the gas processing plant

- 1) to remove
 - impurities,
 - water, and
 - excess hydrocarbon liquid
- 2) to control delivery pressure.

PROCESS MODULES

1. The first unit module is the *physical separation of the distinct phases*, which are typically
 - gas,
 - liquid hydrocarbons,
 - liquid water, and/or
 - solids.

Phase separation of the production stream is usually performed in an inlet separator.

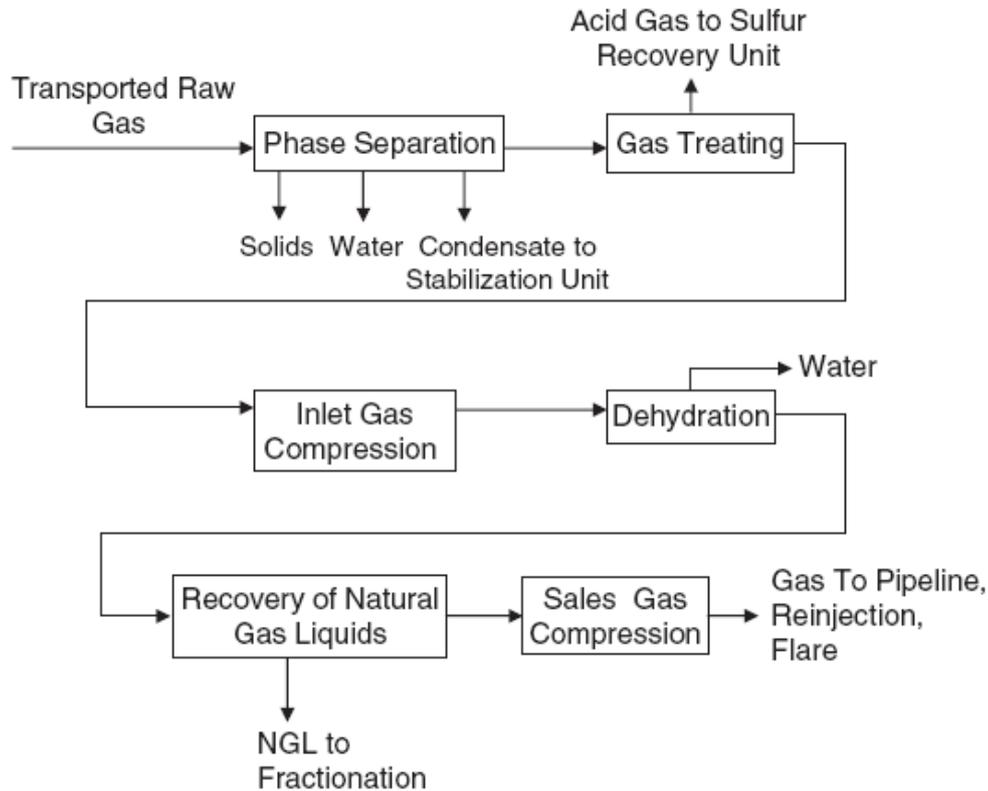


Figure 1. Simplified typical onshore treatment process.

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.

The next step in natural gas processing is *acid gas treating*.

In addition to heavy hydrocarbons and water vapor, natural gas often contains other contaminants that may have to be removed. *Carbon dioxide (CO₂), hydrogen sulfide (H₂S), and other sulfur-containing species such as mercaptans* are compounds that require complete or partial removal. 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.

Depending on the pressure at the plant gate, the next step in processing will either be *inlet compression to an “interstage” pressure*, typically 300–400 psig or be *dew point control and natural gas liquid recovery*.

CONDENSATE STABILIZATION

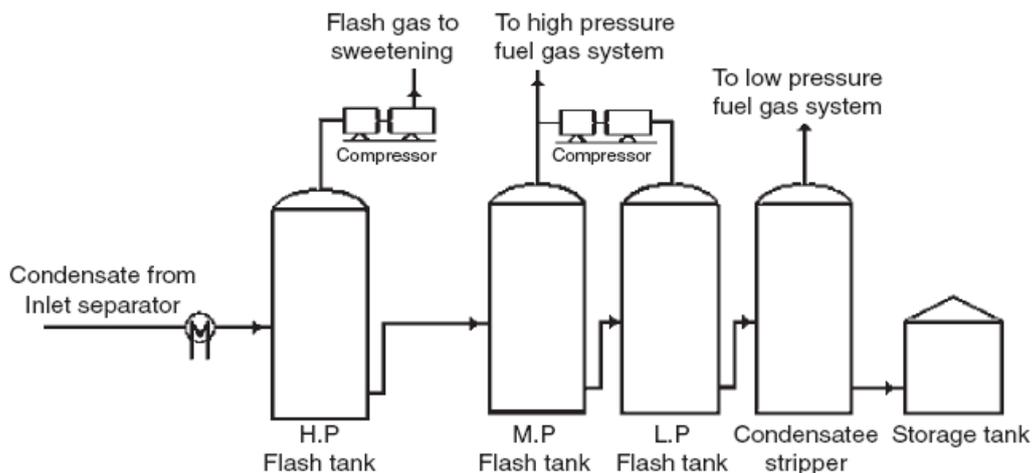
The process of increasing the amount of intermediates (C_3 to C_5) and heavy (C_{+6}) components in the condensate is called “*condensate stabilization*.” In other word, the scope of this process is to separate the very light hydrocarbon gases, methane and ethane in particular, from the heavier hydrocarbon 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 is a simple operation employing only two or three flash tanks. Figure 1 shows a typical scheme of condensate stabilization through the flash vaporization process.



Figure(1): Schematic of 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 is a detailed process, very popular in the industry and precise enough to produce liquids of suitable vapor pressure.

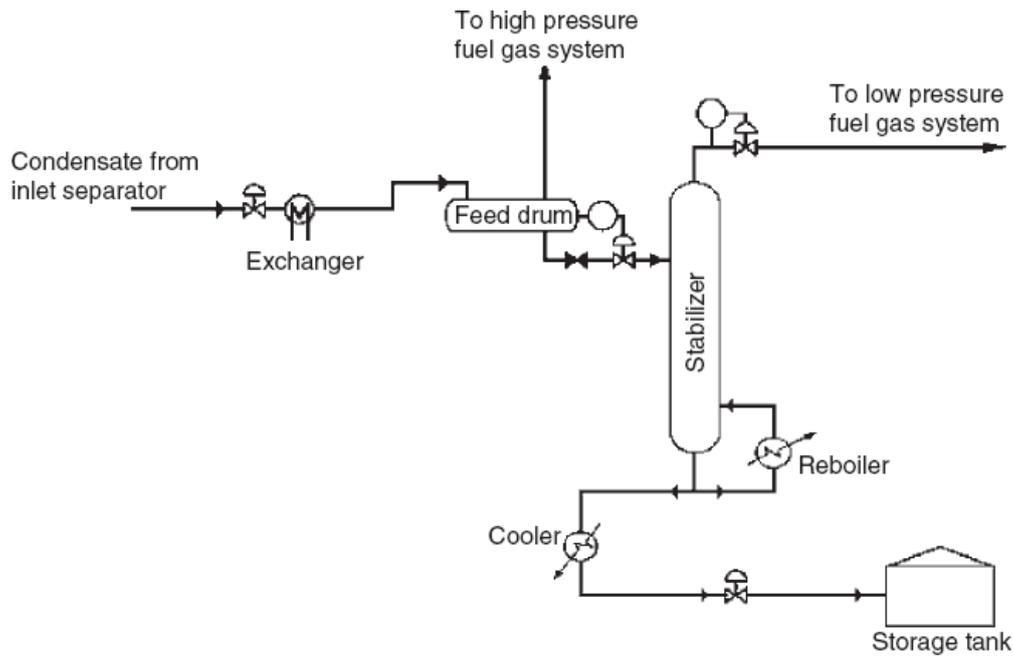


Figure 2: Schematic of a condensate stabilization system.

Design Considerations of Stabilization Column

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.

Figure (3) shows the maximum recommended feed temperature to a stabilizer as a function of operating pressure of the stabilizer.

After the pressure has been chosen and the operating temperatures have been established through use of Figures (3) and (4), the split in the tower must be predicted. There are several methods in which this can be done, but one of the most convenient manual methods involves utilization of pseudo-equilibrium constant (K) values for each component between the top and the bottom of the tower. Using this concept, the separation that can be achieved across a nonrefluxed stabilizer can be estimated by use of the pseudo K values and a simple flash calculation. The vapor from the flash calculation will be the composition of the overhead product, and the liquid from the flash calculation will be the composition of the bottom liquid.

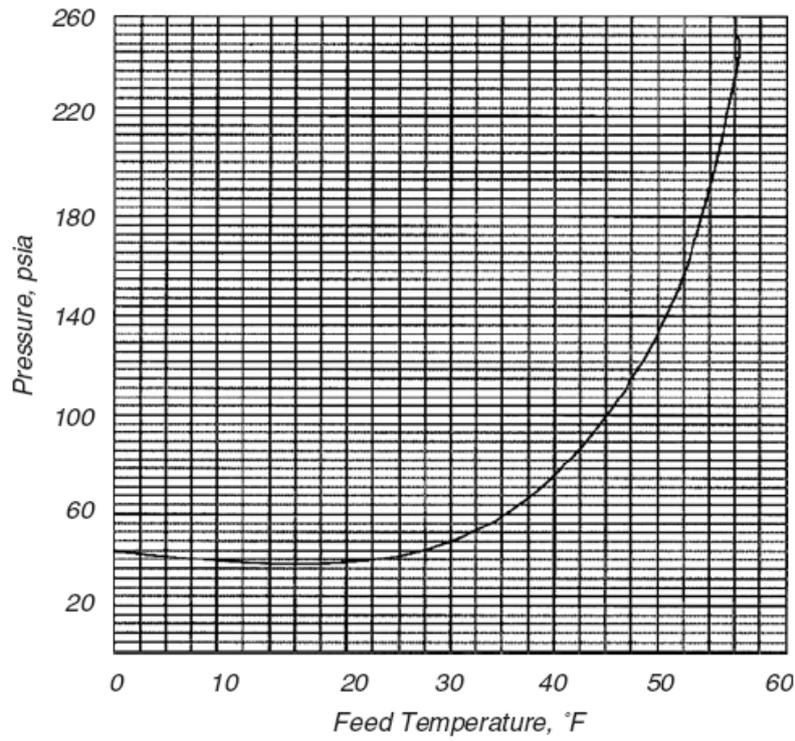


Figure (3): Maximum recommended feed temperature to a cold-feed stabilizer

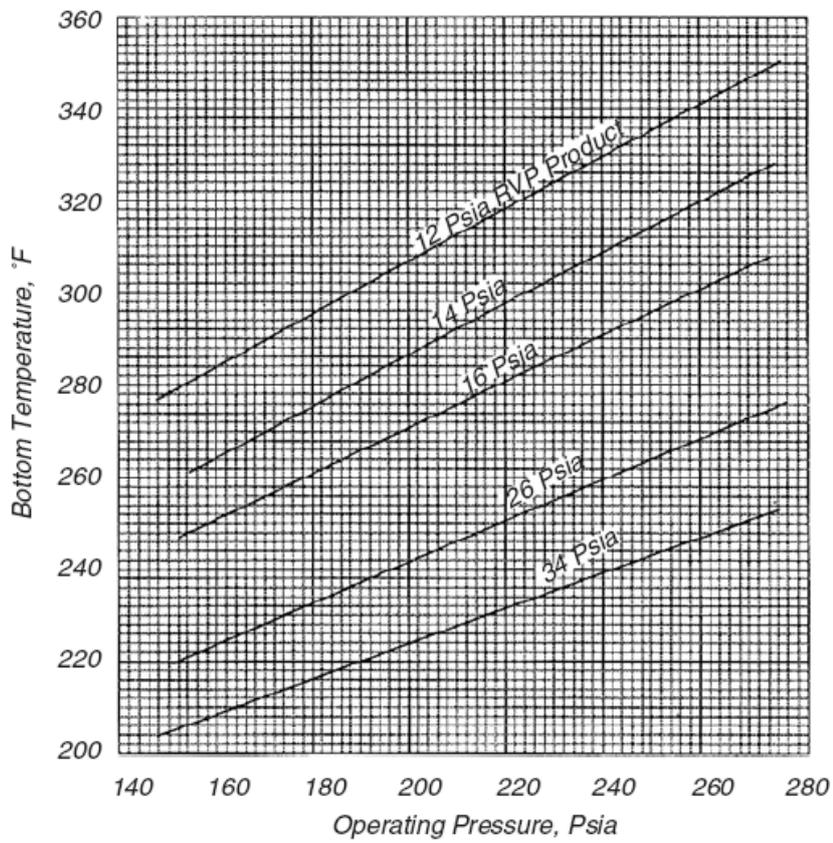


Figure 4: Estimation of proper bottom temperature of a nonrefluxed stabilizer

RVP and Relative Volatility of Various Components (Reid et al., 1977)

Component	RVP psia	Relative volatility
C ₁	5000	96.9
C ₂	800	15.5
C ₃	190	3.68
i-C ₄	72.2	1.40
n-C ₄	51.6	1.00
i-C ₅	20.4	0.40
n-C ₅	15.6	0.30
C ₆	5.0	0.10
C ₇ ⁺	≈0.1	0.00
CO ₂	—	Infinite
N ₂	—	Infinite
H ₂ S	394	7.64

Table(1): RVP and Relative Volatility of Various Components

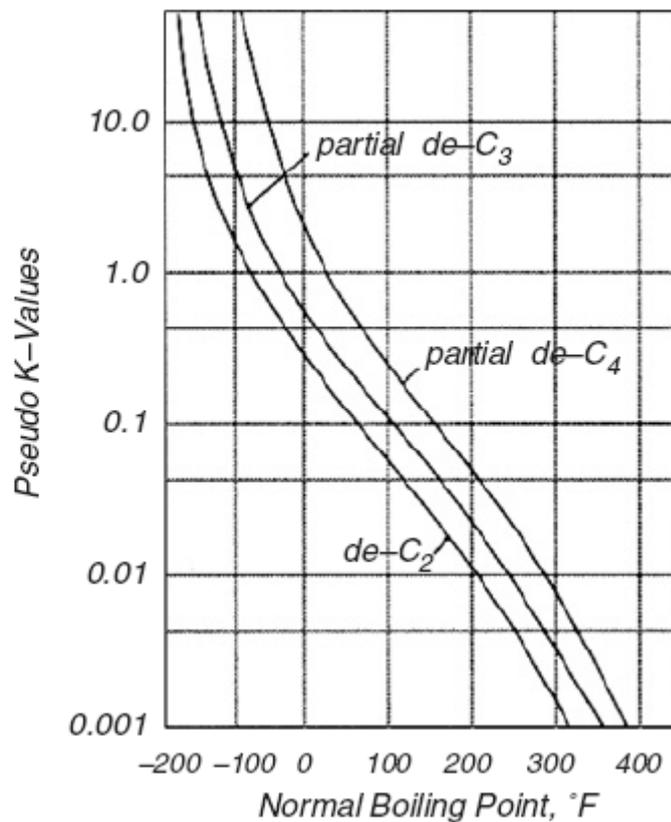


Figure (5): Pseudo K values for cold feed stabilizers

Natural Gas Sweetening

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.
4. The Beavon-Stretford tail gas system.

1- Amine Scrubbing

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.

It is a common unit process used in refineries, petrochemical plants, natural gas processing plants and other industries.

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 (1), includes an *absorber* unit and a *regenerator* unit as well as accessory equipments.

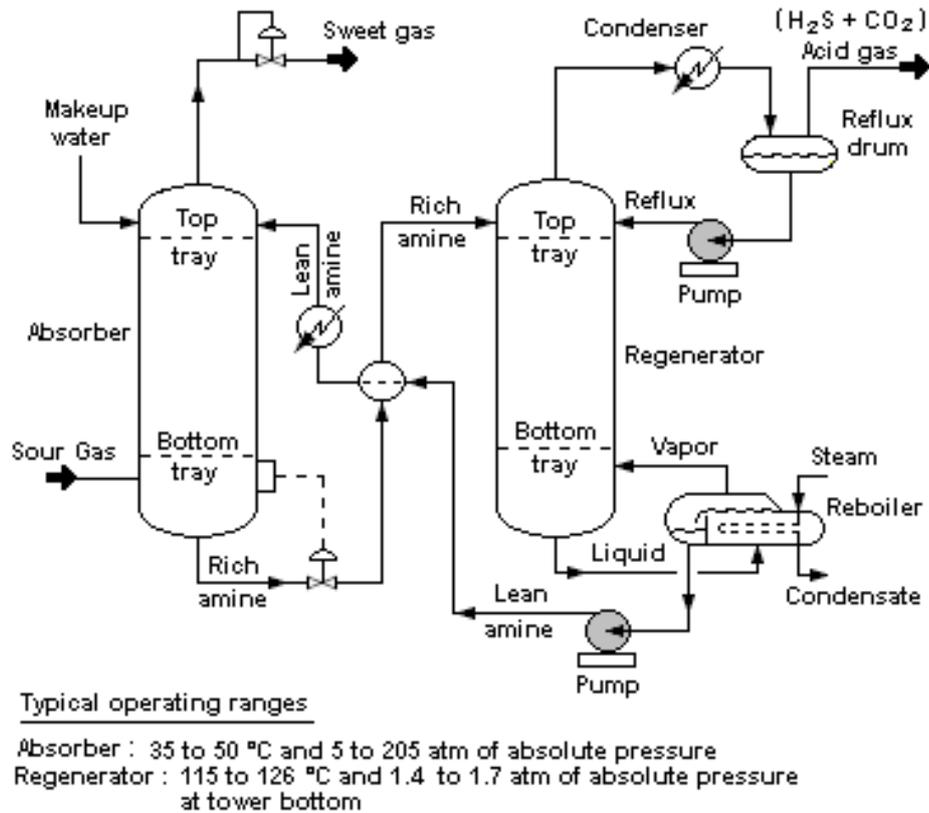


Fig. (2): Process flow diagram of a typical amine treating process

Sulfinol Process

The *Sulfinol process* is a regenerative process developed to reduce H_2S , CO_2 , 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.

Operating Conditions

Very wide ranges of treating pressures and contaminant concentrations can be accommodated. Natural gas pipeline specifications are easily met. Removal of organic sulfur compounds is usually accomplished by the solvent circulations as set by H_2S and CO_2 . In LNG plants a specification of 50 ppm CO_2 prior to liquefaction is attained without difficulty.

Description of the Claus Process

First the H₂S 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 fig.(2).

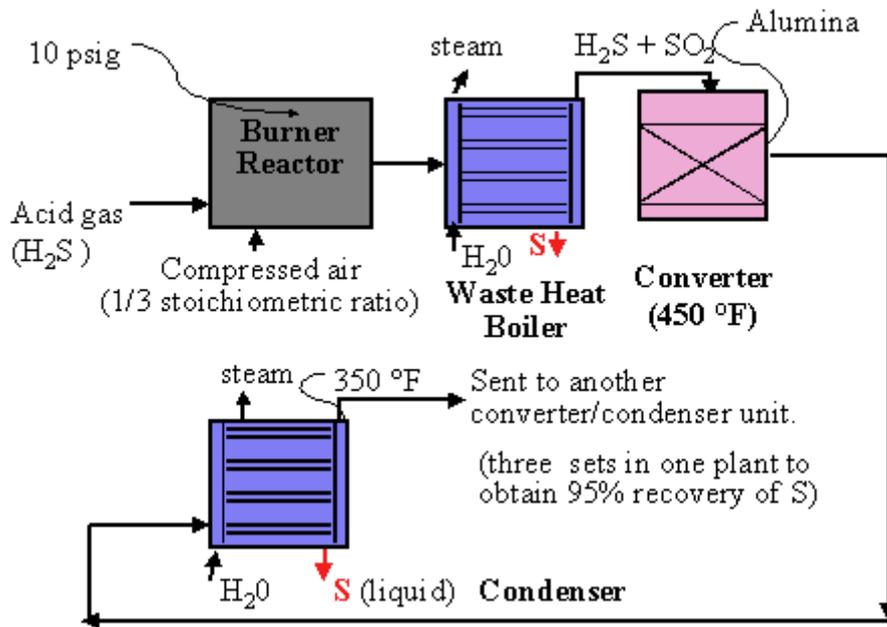
1. **Thermal Step.** The H₂S is partially oxidized with air. This is done in a reaction furnace at high temperatures (1000-1400 deg C). Sulfur is formed, but some H₂S remains unreacted, and some SO₂ is made.



2. **Catalytic Step.** The remaining H₂S is reacted with the SO₂ 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°F > melting point of S to prevent the formation of solid S. Inevitably a small amount of H₂S remains in the tail gas. This residual quantity, together with other trace sulfur compounds, COS and CS₂, 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%.



Converts H₂S to elemental S

Fig. (2) : Claus process

3- Sulfur Plant Tail Gas Clean-Up Processes

Because of the more stringent requirements of pollution control, requirements for tail gas clean-up processes are developed..

✚ SCOT process

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.(3)) 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

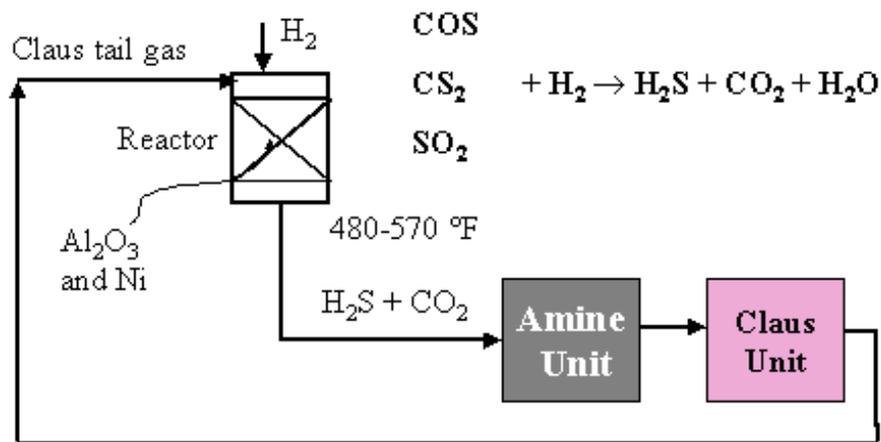
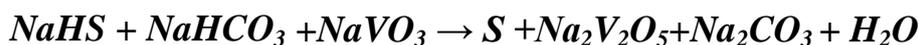
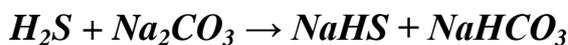


Fig. (3) : SCOT process

4- Beavon Tail Gas Unit

A hydrotreating reactor converts SO_2 in the offgas to H_2S . The generated H_2S is contacted with Stretford solution (a mixture of 2 2 2 vanadium salt, anthraquinone disulfonic acid (ADA), sodium carbonate, and sodium hydroxide) in a liquid-gas absorber. The H_2S reacts stepwise with sodium carbonate and ADA to produce 2 elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber.

Reactions



Gas Dehydration

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. The primary conditions promoting hydration formation are the following:

- Gas must be at or below its water (dew) point with “free” water present.
- Low temperature.
- High pressure.

2. To avoid corrosion problems.

3. Downstream processing requirements. In most commercial hydrocarbon processes, the presence of water may cause side reactions, foaming, or catalyst deactivation. Consequently, purchasers typically require that gas and liquid petroleum gas (LPG) feedstocks meet certain specifications for maximum water content. This ensures that water-based problems will not hamper downstream operations.

Dehydration Methods

Classification of dehydration methods is given in Figure 1.

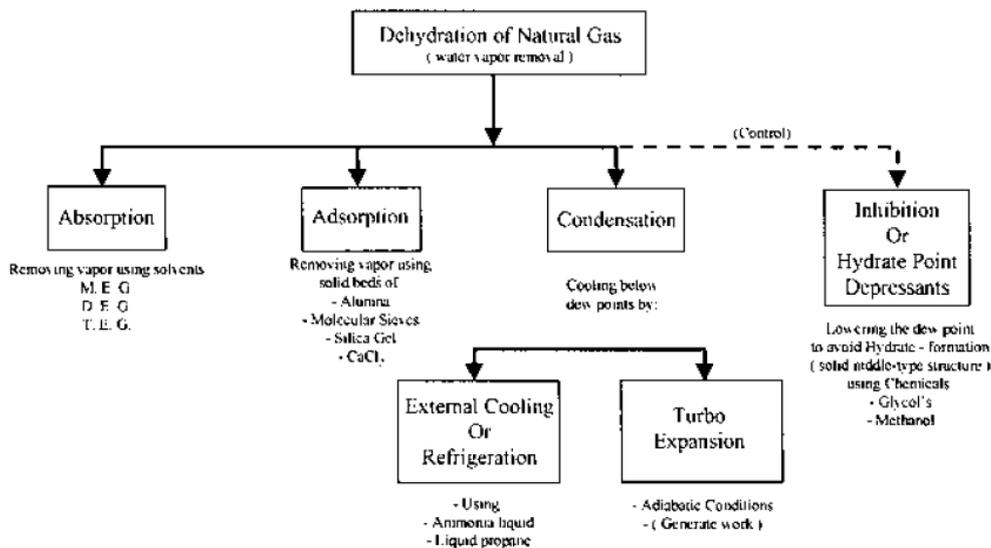


Figure (1): Classification of gas dehydration methods.

ABSORPTION (GLYCOL DEHYDRATION PROCESS)

The basic principles of relevance to the absorption process are as follows:

1. In this process, 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.
2. Absorption, which is defined as the transfer of a component from the gas phase to the liquid phase, is more favorable at a lower temperature and higher pressure. This result is concluded by considering the following relationship (which is a combination of Raoult's law and Dalton's law):

$$\frac{P_i}{P} = \frac{Y_i}{X_i} = K_i$$

where P_i is the pressure of pure component i , P is the total pressure of the gas mixture (system), X_i is the mole fraction of component i in the liquid phase, Y_i is the mole fraction of component i in the vapor phase, and K_i is the equilibrium constant, increasing with temperature and decreasing with pressure.

3. The actual absorption process of water vapor from the gas phase using glycol is dynamic and continuous. Therefore, the gas flow cannot be stopped to let a vapor and the liquid reach an equilibrium condition. Accordingly, the system under consideration must be designed to allow for a close approach to equilibrium while the flow continues.

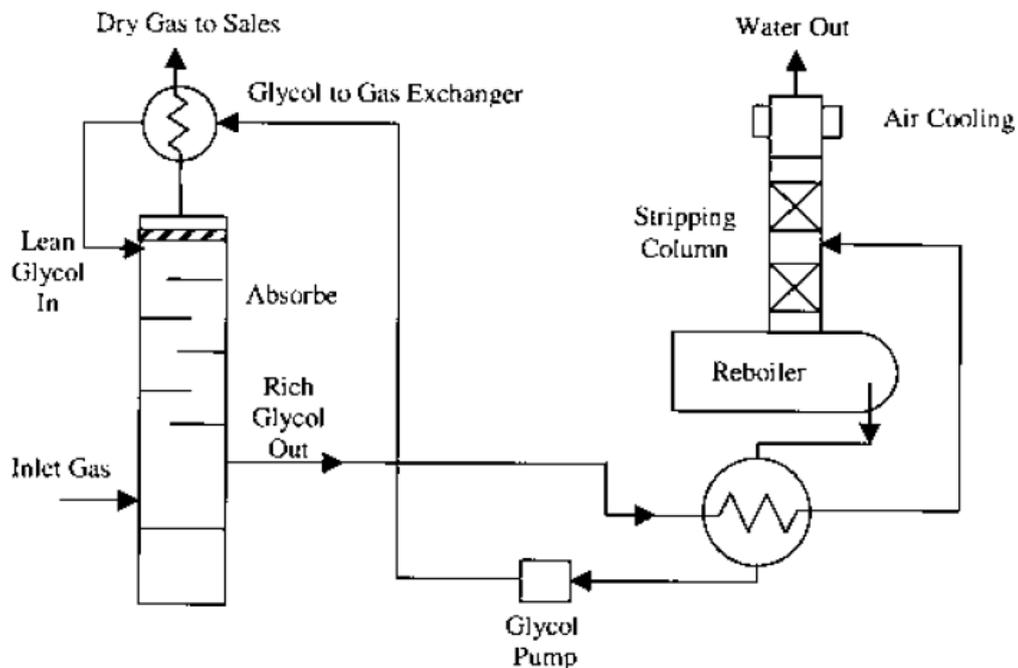


Figure (2): Flow diagram of TEG dehydration

ADSORPTION: SOLID-BED DEHYDRATION

When very low dew points are required, solid-bed dehydration becomes the logical choice. It is based on fixed-bed adsorption of water vapor by a selected desiccant. A number of solid desiccants could be used such as silica gel, activated alumina, or molecular sieves.

The selection of these solids depends on economics. The most important property is the capacity of the desiccant, which determines the loading design expressed as the percentage of water to be adsorbed by the bed. The capacity decreases as temperature increases.

Operation of Solid-Bed Dehydrator

The system may consist of two-bed (as shown in Fig. 3), 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.

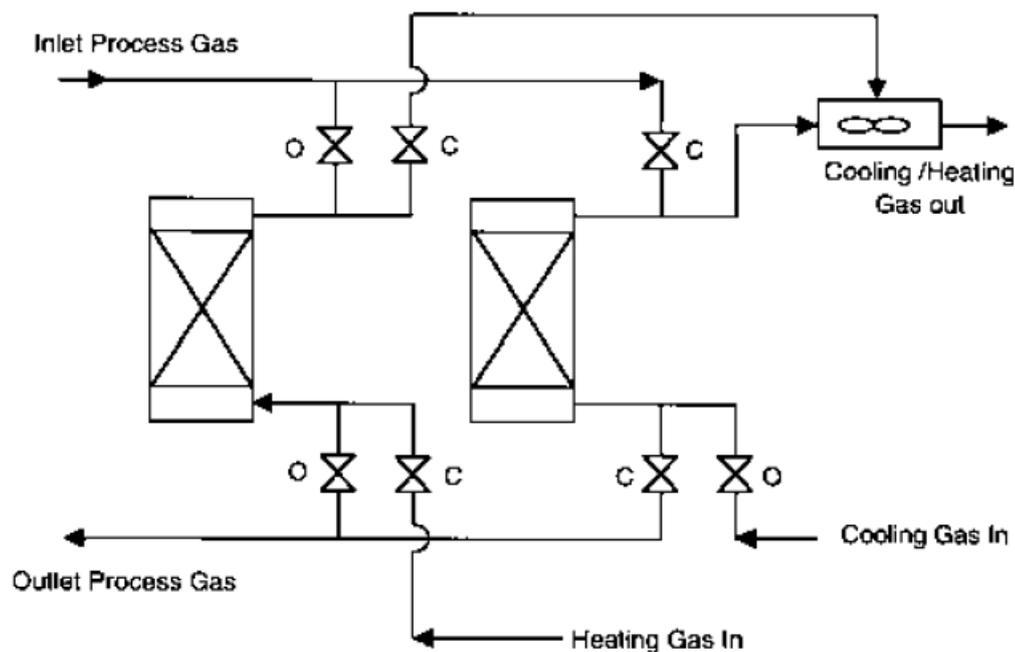


Figure (3): Solid-bed dehydration process.

The feed gas entering the bed from the top and the upper zone becomes saturated first. The second zone is the mass transfer zone (MTZ) and is being loaded. The third zone is still not used and active. The different saturation progress and representation of different zones is shown in Figure (4).

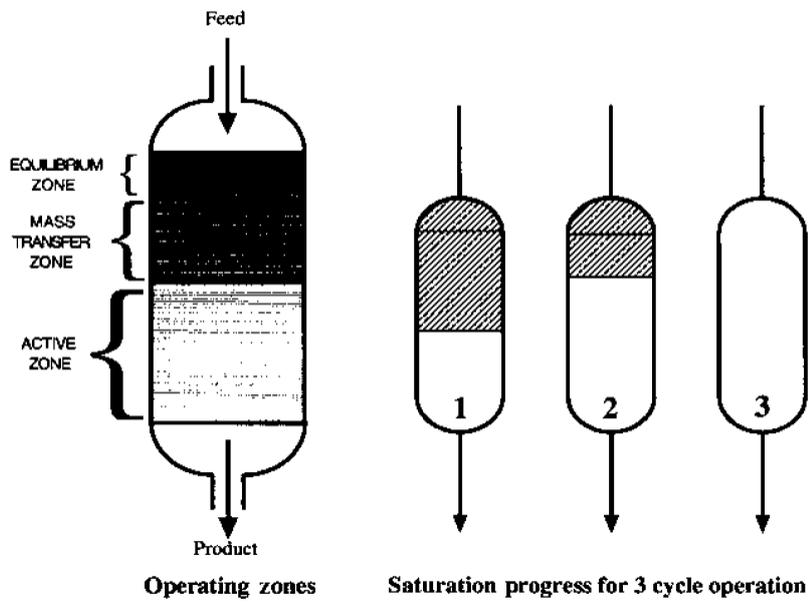


Figure (4): Mode operation.

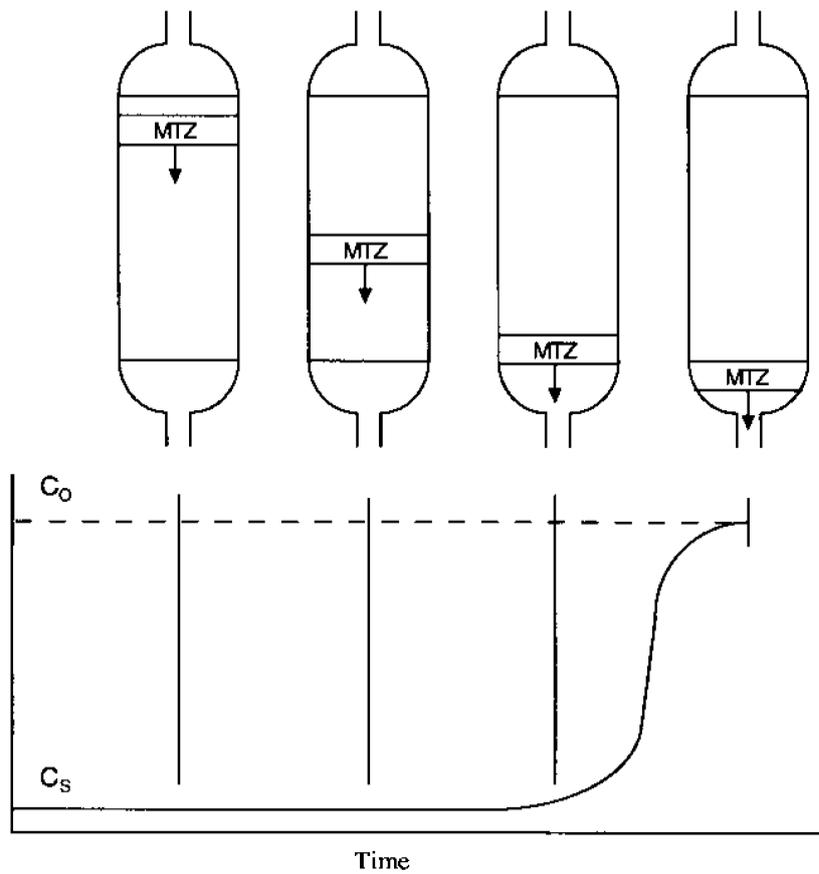


Figure (5): Breakthrough diagram in a fixed bed.

Syngas

Syngas (from *synthesis gas*) is the name given to a gas mixture that contains varying amounts of carbon monoxide and hydrogen generated by the gasification of a carbon containing fuel to a gaseous product with a heating value. Examples include;

- The gasification of coal and in some types of waste-to-energy gasification facilities.
- Steam reforming of natural gas or liquid hydrocarbons to produce hydrogen,

The name comes from their use as;

- intermediates in creating synthetic natural gas (SNG).
- for producing ammonia or methanol.
- Syngas is also used as an intermediate in producing synthetic petroleum for use as a fuel or lubricant via Fischer-Tropsch synthesis and previously the Mobil methanol to gasoline process.

Gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, or biomass, into carbon monoxide and hydrogen by reacting the raw material at high temperatures $> 700\text{ }^{\circ}\text{C}$ with a controlled amount of oxygen (partial combustion). The resulting gas mixture is called synthesis gas or syngas and is itself a fuel. Gasification is a very efficient method for extracting energy from many different types of organic materials, and also has applications as a clean waste disposal technique.

The advantage of gasification is that;

- using the syngas is more efficient than direct combustion of the original fuel; more of the energy contained in the fuel is extracted.
- Syngas may be burned directly in internal combustion engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel.
- Gasification can also begin with materials that are not otherwise useful fuels, such as biomass or organic waste.

- In addition, the high-temperature combustion refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

Gasification of fossil fuels is currently widely used on industrial scales to generate electricity. However, almost any type of organic material can be used as the raw material for gasification, such as wood, biomass, or even plastic waste. Thus, gasification may be an important technology for renewable energy.

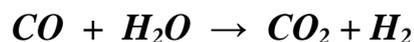
✘ Chemistry

In a gasifier, the carbonaceous material undergoes several different processes:

- The pyrolysis (or devolatilization) process occurs as the carbonaceous particle heats up. Volatiles are released and char is produced, resulting in up to 70% weight loss for coal. The process is dependent on the properties of the carbonaceous material and determines the structure and composition of the char, which will then undergo gasification reactions.
- The combustion process occurs as the volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. Letting **C** represent a carbon-containing organic compound, the basic reaction here is;



- The gasification process occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen, via the reaction;



In addition, the reversible gas phase water gas shift reaction reaches equilibrium very fast at the temperatures in a gasifier. This balances the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen.

Hydrogen production

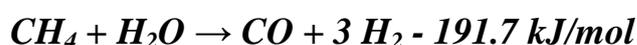
Hydrogen is used for the hydrotreating and hydrocracking processes. The hydrogen from reformer is often not sufficient for hydrotreating process.

Hydrogen is commonly produced from hydrocarbon fossil fuels via a chemical path. Hydrogen may also be extracted from water via biological production in an algae bioreactor, or using electricity (by ***electrolysis***) or heat (by ***thermolysis***); these methods are presently not cost effective for bulk generation in comparison to chemical paths derived from hydrocarbons. Cheap bulk production of hydrogen is a requirement for a healthy hydrogen economy.

Hydrogen can be generated from natural gas with approximately 80% efficiency or other hydrocarbons to a varying degree of efficiency.

1. Steam reforming of natural gas

Commercial bulk hydrogen is usually produced by the steam reforming of natural gas as shown in Fig.(1). At high temperatures (700–1100 °C), steam (H₂O) reacts with methane (CH₄) to yield syngas.

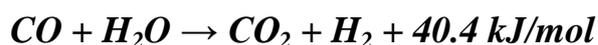


25-40% NiO/low SiO₂/Al₂O₃ catalyst, (760-816°C)

The heat required to drive the process is generally supplied by burning some portion of the methane.

• Shift Conversion

Additional hydrogen can be recovered from the carbon monoxide (CO) through the lower-temperature water gas shift reaction, performed at about 130 °C:



Cr₂O₃ and Fe₂O₃ as catalyst

- **Gas Purification:**

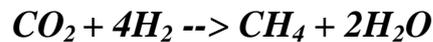
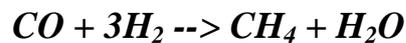
The Shift Converter product stream is then scrubbed, usually through absorption with a potassium carbonate solution to remove the carbon dioxide.

The potassium carbonate solution is regenerated in a Carbon Dioxide Still by applying reboiler heat to the tower bottoms. This heat drives off the carbon dioxide from the solution which is then re-circulated.

- **Methanation**

Since carbon monoxide (CO) and carbon dioxide (CO₂) are poisons to the catalysts of some of the hydrogen consuming refinery processes. Methanation is employed as the final step to remove any remaining CO and CO₂ in the hydrogen stream.

The methanation reaction takes place in a fixed-bed reactor consisting of a nickel-based catalyst. The resulting hydrogen product stream is typically approximately 95% hydrogen and the balance methane with only trace amounts of CO and CO₂. The Methanation reactions are:



Reaction conditions are at 425°F over Ni/Al₂O₃ catalyst.

Trace amounts of CH₄ can be present in the H₂ stream.

