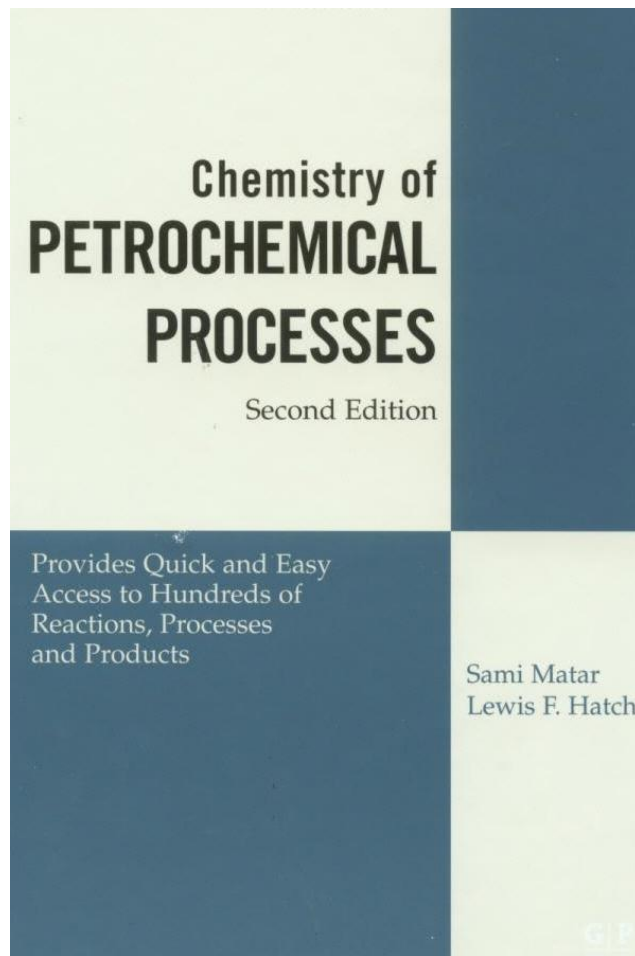# PETROCHEMICALS   LECTURES

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Lecture One

References

Chapter One

Primary Raw Material for Petrochemicals

Introduction

In general, primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered Natural gas and crude oils are the basic raw materials for the manufactureof petrochemicals. Secondary raw materials , or intermediates , are obtained from natural gas and crude oils through different processing schemes . The intermediates may be light hydrocarbon compounds such as methane and ethane , or heavier hydrocarbons mixtures such as naphtha or gas oil. Both naphtha and gas oil are crude oil fractions with different boiling ranges. Coal , oil shale , and tar sand are complex carbonaceous raw materials and possible future energy and chemical sources . However , they must undergo lengthy and extensive processing before they yield fuels and chemicals similar to those produced from crude oils (substitute natural gas (SNG) and synthetic crudes from coal , tar sand and oil shale) .

Natural Gas

(Non- associated and Associated Natural Gases)

Natural gas is naturally occurring mixture of light hydrocarbons accompanied by some non-hydrocarbon compounds . Non – associated natural gas is found in reservoirs containing no oil (dry wells) . Associated gas , on the other hand , is present in contact with and / or dissolved in crude oil and is coproduced with it . The principal component of most natural gases is methane . Higher molecular weight paraffinic hydrocarbons ($C_2 - C_7$) are usually present in smaller amounts with the natural gas mixture , and their ratios vary considerably from one gas field to another .Non – associated gas normally contains a higher methane ratio than associated gas , while the latter contains a higher ratio of heavier hydrocarbons. Table 1-1 shows the analyses of some selected non – associated and associated gases.

Table 1-1
Composition of non − associated and associated natural gases

component	Non – associated gas		ociated gasAss	
	Salt Lake US	Kliffside US	Abqaiq Saudi Arabia	North Sea UK
Methane	95.0	65.8	62.2	85.9
Ethane	0.8	3.8	15.1	8.1
Propane	0.2	1.7	6.6	2.7
Butanes	-----	0.8	2.4	0.9
Pentane and Heavier	-----	0.5	1.1	0.3
Hydrogen Sulfide	------	------	2.8	------
Carbon Dioxide	3.6	------	9.2	1.6
Nitrogen	0.4	25.6	-----	0.5
Helium	------	1.8	------	------

In our discussion ,both non-associated and associated gases will be referred to as natural gas . However , important differences will be noted . The non – hydrocarbon constituents in natural gas vary appreciably from one gas field to another . Some of these compounds are weak acids , such as hydrogen sulfide and carbon dioxide . Others are inert such as nitrogen, helium and argon . Some natural gas reservoirs contain enough helium for commercial production.

Higher molecular weight hydrocarbons present in natural gases are important fuels as well as chemical feed stocks and are normally recovered as natural gas liquids . For example , ethane may be separated for use as a feed stock for steam cracking for the production of ethylene .

Propane and Butane are recovered from natural gas and sold as liquefied petroleum gas (LPG). Before natural gas is used it must be processed or treated to remove the impurities and to recover the heavier hydrocarbons (heavier than methane) . The 1998 U.S. gas consumption was approximately 22.5 trillion ft^3 .

Natural Gas Treatment Processes

Raw natural gases contain variable amounts of carbon dioxide , hydrogen sulfide, and water vapor. The presence of hydrogen sulfide in natural gas for domestic consumption cannot be tolerated because it is poisonous . It also corrodes metallic equipment. Carbon dioxide is undesirable , because it reduces the heating value of the gas and solidifies under the high pressure and low temperatures used for transporting natural gas . For obtaining a sweet , dry natural gas , acid gases must be removed and water vapor reduced. In addition , natural gas with appreciable amounts of heavy hydrocarbons should be treated for their recovery as natural gas liquids .

Acid Gas Treatment

Acid gases can be reduced or removed by one or more of the following methods:

1-Physical absorption using a selective absorption solvent .

2-Physical adsorption using a solid adsorbent.

3- Chemical absorption where a solvent (a chemical) capable of reacting reversibly with the acid gases is used .

Physical Absorption

In these processes , no chemical reaction occurs between the acid gas and the solvent . The solvent , or absorbent , is a liquid that selectively absorbs the acid gases and leaves out the hydrocarbons . For example , the solvent is dimethyl ether of polyethylene glycol . Raw natural gas passes countercurrently to the descending solvent . When the solvent becomes saturated with the acid gases , the pressure is reduced , and hydrogen sulfide and carbon dioxide are desorbed . The solvent is then recycled to the absorption tower.

Physical Adsorption

In these processes, a solid with a high surface area is used . Molecular sieves (zeolites) are widely used and are capable of adsorbing large amounts of gases . In practice , more than one adsorption bed is used for continuous operation . One bed is in use while the other is being regenerated . Regeneration is accomplished by passing hot dry fuel gas through the bed. Molecular sieves are competitive only when the quantities of hydrogen sulfide and carbon dioxide are low .

Molecular sieves are also capable of adsorbing water in addition to the acid gases .

Chemical Absorption (Chemisorption)

These processes are characterized by a high capability of absorbing large amounts of acid gases . They use a solution of a relatively weak base , such as monoethanolamine . The acid gas forms a weak bond with the base which can be regenerated easily . Mono- and diethanolamines are frequently used for this purpose . The amine concentration normally ranges between 15 and 30% . Natural gas is passed through the amine solution where sulfides , carbonates , and bicarbonates are formed . Diethanolamine is a favored absorbent due to its lower corrosion rate , smaller amine loss potential , fewer utility requirements , and minimal reclaiming needs.   Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS) , while the mono – reacts irreversibly with 95% of the COS and forms a degradation product that must be disposed of .
Diglycolamine (DGA) , is another amine solvent used. Diglycolamine solutions are characterized by low freezing points, which make them suitable for use in cold climates .

Strong basic solutions are effective solvents for acid gases . However , these solutions are not normally used for treating large volumes of natural gas because the acid gases form stable salts , which are not easily regenerated . For example , carbon dioxide and hydrogen sulfide react with aqueous sodium hydroxide to yield sodium carbonate and sodium sulfide , respectively.

$$CO_2 + 2\ NaOH\ (aq) \longrightarrow Na_2Co_3 + H_2O$$

$$H_2S + 2\ NaOH\ (aq) \longrightarrow Na_2S + 2H_2O$$
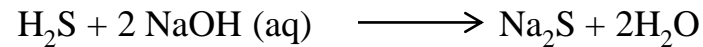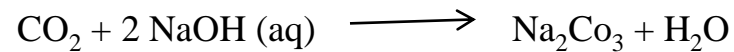
However , a strong caustic solution is used to remove mercaptans from gas and liquid streams . The caustic solution is then recycled for regeneration   .

Water Removal

Moisture must be removed from natural gas to reduce corrosion problems and to prevent hydrate formation . Hydrate are solid white compounds formed from a physical – chemical reaction between hydrocarbons and water under the high pressures and low temperatures used to transport natural gas via pipeline . Hydrates reduce pipeline efficiency .

To prevent hydrate formation , natural gas may be treated with glycols , which dissolve water efficiently . Ethylene glycol (EG) , diethylene glycol (DEG) , and triethylene glycol (TEG) are typical solvents for water removal . Triethylene glycol is preferable in vapor phase processes because of its low vapor pressure , which results in less glycol loss . The TEG absorber normally contains 6 to 12 bubble- cap trays to accomplish the water absorption . However , more contact stages may be required to reach dew points below -40°F . Calculations to determine the number of trays or feet of packing , the required glycol concentration , or the glycol circulation rate require vapor – liquid equilibrium data . Predicting the interaction between TEG and water vapor in natural gas over a broad range allows the designs for ultra-low dew point applications to be made .

Another way to dehydrate natural gas is by injecting methanol into gas lines to lower the hydrate-formation temperature below ambient . Water can also be reduced or removed from natural gas by using solid adsorbents such as molecular sieves or silica gel .

Condensable Hydrocarbon Recovery

Hydrocarbons heavier than methane that are present in natural gases are valuable raw materials and important fuels . They can be recovered by lean oil extraction. The first step in this scheme is to cool the treated gas by exchange with liquid propane . The cooled gas is then washed with a cold hydrocarbon liquid , which dissolves most of the condensable hydrocarbons . The uncondensed gas is dry natural gas and is composed mainly of methane with small amounts of ethane and heavier hydrocarbons . The condensed hydrocarbons or natural gas liquids (NGL) are stripped from the rich solvent , which is recycled . Table 1-2 compares the analysis of natural gas before and after treatment. Dry natural gas may then be used either as a fuel or as a chemical feedstock .

Another way to recover NGL is through cryogenic cooling to very low temperatures (-150 to -180 ^{o}F), which are achieved primarily through adiabatic expansion of the inlet gas . The inlet gas is first treated to remove water and acid gases , then cooled via heat exchange and refrigeration . Further cooling of the gas is accomplished through turbo expanders , and the gas is sent to a demethanizer to separate methane from NGL . Improved NGL recovery could be achieved through better control strategies and use of on-line gas chromatographic analysis .

Table 1-2
Typical analysis of natural gas before and after treatment

Component mol%	Feed	Pipeline gas
N_2	0.45	**0.62**
CO_2	27.85	**3.50**
H_2S	0.0013	**-------**
C_1	70.35	**94.85**
C_2	0.83	**0.99**
C_3	0.22	**0.003**
C_4	0.13	**0.004**
C_5	0.06	**0.004**

Natural Gas Liquids (NGL)

Natural gas liquids(condensable hydrocarbons) are those hydrocarbons heavier than methane that are recovered from natural gas . The amount of NGL depends mainly on the percentage of the heavier hydrocarbons present in the gas and on the efficiency of the process used to recover them . (A high percentage is normally expected from associated gas .)
Natural gas liquids are normally fractionated to separate them into three streams :

1-An ethane- rich stream , which is used for producing ethylene .

2-Liquefied petroleum gas (LPG) , which is a propane – butane mixture . It is mainly used as a fuel or a chemical feedstock . Liquefied petroleum gas is evolving into an important feedstock for olefin production . It has been predicted that the world (LPG) market for chemicals will grow from 23.1 million tons consumed in 1988 to 36.0 million tons by the year 2000 .

3-Natural gasoline (NG) is mainly constituted of C_{5+} hydrocarbons and is added to gasoline to raise its vapor pressure . Natural gasoline is usually sold according to its vapor pressure .

Natural gas liquids may contain significant amounts of cyclohexane , a precursor for nylon 6. Recovery of cyclohexane from NGL by conventional distillation is difficult and not economical because heptane isomers are also present which boil at temperatures nearly identical to that of cyclohexane . An extractive distillation process has been recently developed to separate cyclohexane .

Liquefied Natural Gas (LNG)

After the recovery of natural gas liquids , sweet dry natural gas may be liquefied for transportation   through cryogenic tankers . Further treatment may be required to reduce the water vapor below 10 ppm and carbon dioxide and hydrogen sulfide to less than 100 and 50 ppm , respectively .

Two methods are generally used to liquefy natural gas : the expander cycle and mechanical refrigeration . In the expander cycle , part of the gas is expanded from a high transmission pressure to a lower pressure . This lowers the temperature of the gas . Trough heat exchange , the cold gas cools the incoming gas , which in a similar way cools more incoming gas until the liquefaction temperature of methane is reached

In mechanical refrigeration , a multicomponent refrigerant consisting of nitrogen , methane , ethane , and propane is used through a cascade cycle. When these liquids evaporate , the heat required is obtained from natural gas , which loses energy / temperature till it is liquefied . The refrigerant gases are recompressed and recycled . Table 1-3 lists important properties of a representative liquefied natural gas mixture.

Table 1-3
Important properties of a representative liquefied natural gas mixture

Density , lb/cf	27.00
Boiling point , °C	-158
Calorific value , Btu/lb	21200
Specific volume , cf/lb	0.037
Critical temperature , °C*	-82.3
Critical pressure , psi*	-673

*Critical temperature and pressure for pure liquid methane