NATIONAL OPEN UNIVERSITY OF NIGERIA

CHM 306

Petroleum Chemistry

Module 2

CHM 306 Petroleum Chemistry Module 2

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Published in 2021 by the National Open University of Nigeria

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Module 2 Composition of Crude Oil and Natural Gas

Unit 1 Composition, Properties and Classification of Crude Oil

1.0 Introduction

The exact nature of crude oil varies, quite widely, from oil field to oil field but, on average, it has a hydrogen content of about 12% by weight and a carbon content approaching 88% by weight. The remainder is mainly sulphur and nitrogen. In most cases there are hundreds of different chemical compounds in a sample of crude oil, but they nearly all have the common property of containing only carbon and hydrogen.

This unit examines the composition of crude oil, its properties which distinguish it from natural gas. The different classification of crude oil will also be examined.

2.0 Objectives

At the end of this unit, you should be able to:

- explain the composition of crude oil
- state the properties of crude oil
- enumerate the various types of crude oil.

3.0 Main Content

3.1 Composition of Crude Oil

The crude oil mixture is composed of the following:

- Hydrocarbon compounds (compounds made of carbon and hydrogen only).
- Non-hydrocarbon compounds.
- Organometallic compounds and inorganic salts (metallic compounds).

3.2 Hydrocarbon Compounds

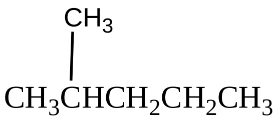
The principal constituents of crude oil are hydrocarbon compounds. All hydrocarbon classes are present in the crude mixture, except alkenes and alkynes. This may indicate that crude oil originated under a reducing atmosphere. The following is a brief description of the different hydrocarbon classes found in all crude oil.

3.2.1 Alkanes (paraffins)

Alkanes are saturated hydrocarbons having the general formula C_nH_{2n+2}. The simplest alkane, methane (CH_4), is the principal constituent of natural gas. Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oil in a dissolved state. Normal alkanes (n-alkanes, n-paraffins) are straight-chain hydrocarbons having no branches. Branched alkanes are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain. A branched alkane with the same number of carbons and hydrogens as an n-alkane is called an isomer. For example, butane (C_4H_{10}) has two isomers, n-butane and 2-methyl propane (isobutane). As the molecular weight of the hydrocarbon increases, the number of isomers also increases. Pentane (C_5H_{12}) has three isomers; hexane (C_6H_{14}) has five. The following shows the isomers of hexane:

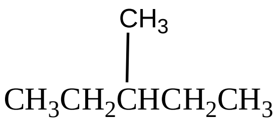
$CH_3(CH_2)_4CH_3$

n-Hexane



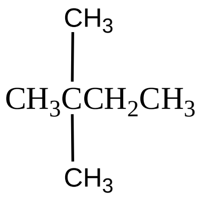
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

2-Methylpentane
isohexane



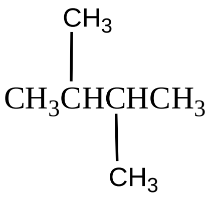
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

3-Methylpentane



$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_3$

2,2-dimethylbutane



$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_3$

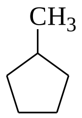
2,3-dimethylbutane

An isoparaffin is an isomer having a methyl group branching from carbon number 2 of the main chain. Crude oil contains many short, medium, and long-chain normal and branched paraffins. A naphtha fraction (obtained as a light liquid stream from crude fractionation) with a narrow boiling range may contain a limited but still large number of isomers.

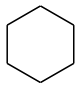
3.2.2 Cycloparaffins (Naphthenic)

Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oil. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds. They are normally present in the light and the heavy naphtha fractions. Cyclohexanes, substituted cyclopentanes, and substituted cyclohexanes are important precursors for aromatic hydrocarbons.

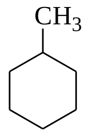
The examples shown here are for three naphthenes of special importance. If a naphtha fraction contains these compounds, the first two can be converted to benzene, and the last compound can dehydrogenate to toluene during processing. Dimethylcyclohexanes are also important precursors for xylenes (see “Xylenes” later in this section).Heavier petroleum fractions such as kerosine and gas oil may contain two or more cyclohexane rings fused through two vicinal carbons.



Methylcyclopentane



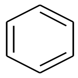
Cyclohexane



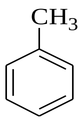
Methylcyclohexane

3.2.3 Aromatic Compounds

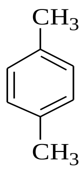
Lower members of aromatic compounds are present in small amounts in crude oil and light petroleum fractions. The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oil. Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components. Separating BTX aromatics from crude oil distillates is not feasible because they are present in low concentrations. Enriching a naphtha fraction with these aromatics is possible through a catalytic reforming process. Binuclear aromatic hydrocarbons are found in heavier fractions than naphtha. Trinuclear and polynuclear aromatic hydrocarbons, in combination with heterocyclic compounds, are major constituents of heavy crude and crude residues. Asphaltenes are a complex mixture of aromatic and heterocyclic compounds. The nature and structure of some of these compounds have been investigated. The following are representative examples of some aromatic compounds found in crude oil:



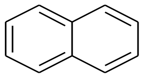
Benzene



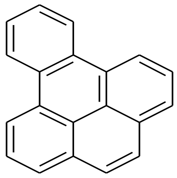
Toluene



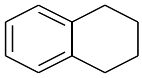
p-Xylene



Naphthalene



1,2-Benzopyrene



Tetralin

Self-Assessment Exercise

1. What are the principal constituents of crude oil?
2. Crude oil is composed of how many groups of compounds? Name the groups
3. What is the difference between n-paraffins and isoparaffins?

3.2.4 Non-Hydrocarbon Compounds

Various types of non-hydrocarbon compounds occur in crude oil and refinery streams. The most important are the organic sulphur, nitrogen, and oxygen compounds. Traces of metallic compounds are also found in crude oil. The presence of these impurities is harmful and may cause problems to certain catalytic processes. Fuels having high sulphur and nitrogen levels cause pollution problems in addition to the corrosive nature of their oxidization products.

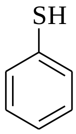
3.2.5 Sulphur Compounds

Sulphur in crude oil is mainly present in the form of organic sulphur compounds. Hydrogen sulphide is the only important inorganic sulphur compound found in crude oil. Its presence, however, is harmful because of its corrosive nature. Organic sulphur compounds may generally be classified as acidic and non-acidic. Acidic sulphur compounds are the thiols (mercaptans). Thiophene, sulphides, and disulphides are examples of non-acidic sulphur compounds found in crude fractions. Extensive research has been carried out to identify some sulphur compounds in a narrow light petroleum fraction. Examples of some sulphur compounds from the two types are:

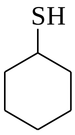
Acidic Sulphur compounds

CH_3SH

Methylmercaptan



Phenylmercaptan



Cyclohexylthiol

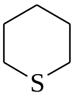
Non -acidic Sulphur compounds

CH_3SCH_3

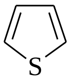
Dimethyl sulphide

$CH_3S\text{-}SCH_3$

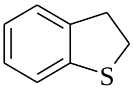
Dimethyldisulphide



Thiocyclohexane



Thiophene



Benzothiophene

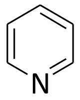
Sour crude oil contains a high percentage of hydrogen sulphide. Because many organic sulphur compounds are not thermally stable, hydrogen sulphide is often produced during crude processing. High-sulphur crudes are less desirable because treating the different refinery streams for acidic hydrogen sulphide increases production costs. Most sulphur compounds can be removed from petroleum streams through hydro treatment processes, where hydrogen sulphide is produced and the corresponding hydrocarbon released. Hydrogen sulphide is then absorbed in a suitable absorbent and recovered as sulphur.

3.2.6 Nitrogen Compounds

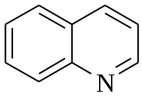
Organic nitrogen compounds occur in crude oil either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin. The nitrogen content in most crude oil is very low and does not exceed 0.1 weight per cent. In some heavy crude, however, the nitrogen content may reach up to 0.9 weight per cent. Nitrogen compounds are more thermally stable than sulphur compounds and accordingly are concentrated in heavier petroleum fractions and residues. Light petroleum streams may contain trace amounts of nitrogen compounds, which should be removed because they poison many processing catalysts. During hydro treatment of petroleum fractions, nitrogen compounds are hydrogenated to ammonia and the corresponding hydrocarbon. For example, pyridine is denitrogenated to ammonia and pentane:

Nitrogen compounds in crude may generally be classified into basic and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure. Both pyridine and pyrrole are stable compounds due to their aromatic nature. The following are examples of organic nitrogen compounds.

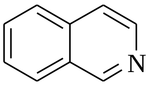
Basic Nitrogen Compounds



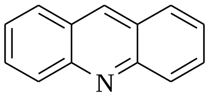
Pyridine



Quinoline



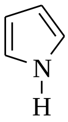
Isoquinoline



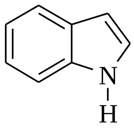
Acridine

Porphyrins are non-basic nitrogen compounds. The porphyrin ring system is composed of four pyrrole rings joined by =CH-groups. The entire ring system is aromatic. Many metal ions can replace the pyrrole hydrogens and form chelates. The chelate is planar around the metal ion and resonance results in four equivalent bonds from the nitrogen atoms to the metal. Almost all crude oil and bitumen contain detectable amounts of vanadyl and nickel porphyrins.

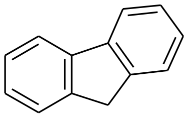
Non-Basic Nitrogen Compounds



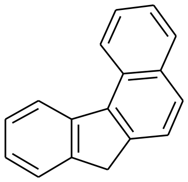
Pyrrole



Indole



Carbazole



Benzocarbazole

Separation of nitrogen compounds is difficult, and the compounds are susceptible to alteration and loss during handling. However, the basic low molecular weight compounds may be extracted with dilute mineral acids.

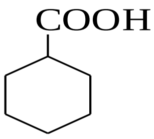
3.2.7 Oxygen Compounds

Oxygen compounds in crude oil are more complex than the sulphur compounds. However, their presence in petroleum streams is not poisonous to processing catalysts. Many of the oxygen compounds found in crude oil are weakly acidic. They are carboxylic acids, cresylic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain. Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crude is generally low, but may reach as much as 3% , as in some California crude. Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds. They are of no commercial value. The following shows some of the oxygen compounds commonly found in crude oil:

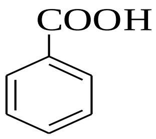
Acidic Oxygen Compounds

$CH_3(CH_2)_nCOOH$

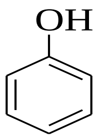
An aliphatic acid



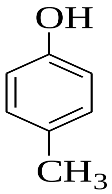
Cyclohexane carboxylic acid



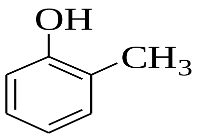
Aromatic acid



Phenol



Para cresylic acid



Ortho cresylic acid

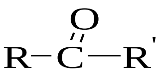
Non-Acidic Oxygen Compounds

$R—COOR'$

Esters

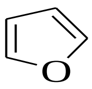
$RCONHR$

Amides

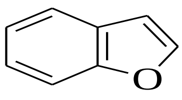


$R-\overset{O}{\overset{\|}{C}}-R'$

Ketone



Furan



Benzofuran

3.2.8 Metallic Compounds

Many metals occur in crude oil. Some of the more abundant are sodium, calcium, magnesium, aluminium, iron, vanadium, and nickel. They are present either as inorganic salts, such as sodium and magnesium chlorides, or in the form of organometallic compounds, such as those of nickel and vanadium (as in porphyrins). Calcium and magnesium can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable. Although metals in crude are found in trace amounts, their presence is harmful and should be removed. When crude oil is processed, sodium and magnesium chlorides produce hydrochloric acid, which is very corrosive. Desalting crude oil is a necessary step to reduce these salts. Vanadium and nickel are poisons to many catalysts and should be reduced to very low levels. Most of the vanadium and nickel compounds are concentrated in the heavy residues. Solvent extraction processes are used to reduce the concentration of heavy metals in petroleum residues.

3.3 Properties of Crude Oil

Crude oil differs appreciably in their properties according to origin and the ratio of the different components in the mixture. Lighter crude oil generally yields more valuable light and middle distillates and are sold at higher prices. Crude oil containing a high per cent of impurities, such as sulphur compounds, are less desirable than low-sulphur crude oil because of their corrosive properties and the extra treating cost. Corrosive properties of crude oil is a function of many parameters among which are the type of sulphur compounds and their decomposition temperatures, the total acid number, the type of carboxylic and naphthenic acids in the crude oil and their decomposition temperatures. It was found that naphthenic acids begin to decompose at 600°F. Refinery experience has shown that above 750°F, there is no naphthenic acid corrosion.

For a refiner, it is necessary to establish certain criteria to relate one crude oil to another to be able to assess its quality and choose the best processing scheme. The following are some of the important tests used to determine the properties of crude oil.

3.3.1 Density, Specific Gravity and API Gravity

Density is defined as the mass of unit volume of a material at a specific temperature. A more useful unit used by the petroleum industry is specific gravity, which is the ratio of the weight of a given volume of a material to the weight of the same volume of water measured at the same temperature. Specific gravity is used to calculate the mass of crude oil and its products. Usually, crude oil and their liquid products are first measured on a volume basis, and then changed to the corresponding masses using the specific gravity. The API (American Petroleum Institute) gravity is another way to express the relative masses of crude oil. The API gravity could be calculated mathematically using the following equation:

$$\boldsymbol{o}_{API} = \frac{141.5}{\boldsymbol{Sp.gr.}^{60}/_{60^o}} - 131.5$$

A low API gravity indicates a heavier crude oil or a petroleum product, while a higher API gravity means a lighter crude oil or product. Specific gravities of crude oil roughly range from 0.82 for lighter crude to over 1.0 for heavier crude.

3.3.2 Salt Content

The salt content expressed in milligrams of sodium chloride per liter oil (or in pounds/barrel) indicates the amount of salt dissolved in water. Water in crude oil is mainly present in an emulsified form. A high salt content in a crude oil presents serious corrosion problems during the refining process. In addition, high salt content is a major cause of plugging heat exchangers and heater pipes. A salt content higher than 10 lb/1,000 barrels (expressed as NaCl) requires desalting.

3.3.3 Sulphur Content

Determination of the sulphur content in crude oil is important because the amount of sulphur present indicates the type of treatment required for the distillates. To determine sulphur content, a weighed crude sample (or fraction) is burned in an air stream. All sulphur compounds are oxidised to sulphur dioxide, which is further oxidised to sulphur trioxide and finally titrated with a standard alkali. Identifying sulphur compounds in crude oil and their products is of little use to a refiner because all sulphur compounds can easily be desulphurised by hydrogen to hydrogen sulphide and the corresponding hydrocarbon. The sulphur content of crude, however, is important and is usually considered when determining commercial values.

3.3.4 Pour Point

The pour point of a crude oil or product is the lowest temperature at which oil is observed to flow under the conditions of the test. Pour point data indicates the amount of long-chain paraffins (petroleum wax) found in a crude oil. Paraffinic crude usually have higher wax content than other crude types. Handling and transporting crude oil and heavy fuels is difficult at temperatures below their pour points often, chemical additives known as pour point depressants are used to improve the flow properties of the fuel. Long-chain n-paraffins ranging from 16–60 carbon atoms in particular, are responsible for near-ambient temperature precipitation. In middle distillates, less than 1% wax can be sufficient to cause solidification of the fuel.

3.3.5 Ash Content

This test indicates the amount of metallic constituents in a crude oil. The ash left after completely burning an oil sample usually consists of stable metallic salts, metal oxides, and silicon oxide. The ash could be further analysed for individual elements using spectroscopic techniques.

3.4 Crude Oil Classification

Various crude oil classifications have been proposed by geochemists and petroleum refiners. The interests of the geochemists and petroleum refiners are different. In addition, the physical and/or chemical parameters used in the classifications are different.

Petroleum refiners are mostly interested in the amount of the successive distillation fraction e.g. gasoline, naphtha, kerosene, gas, oil, lubricating distillate, and the chemical composition or physical properties of these fractions *viz-a-viz* viscosity, cloud test etc.

Geochemist and geologist are more interested in identifying and characterising the crude oil in order to relate them to the source rocks and to measure their grade of evolution. As a result they rely on the chemical and structural information of crude oil constituents, especially on the molecules which are suppose to convey genetic information. Therefore, molecules at relatively low concentrations, such as high molecular weight n-alkanes, steroids and terpenes, may be of great interest to geochemist and geologist.

Appreciable property differences appear between crude oil as a result of the variable ratios of the crude oil components. For a refiner dealing with crudes of different origins, a simple criterion may be established to group crudes with similar characteristics. Crude oil can be arbitrarily classified into three or six groups depending on the relative ratio of the hydrocarbon classes that predominate in the mixture. The following describes six types of crudes:

- Paraffinic.
- Paraffinic - naphthenic
- Naphthenic.
- Aromatic-Intermediate.
- Aromatic - asphaltic
- Aromatic – naphthenic.

3.4.1 Paraffinic Class

This class of petroleum is generated in delta or coastal sediments of the continental margins, or in non-marine source bed and is comprised of light crude oil, some being fluid and some high-wax, high-pour point crude oil. The viscosity of these high-pour point oils at room temperature is high, due to a high content of n-alkanes (>20). At slightly elevated temperature of between 35-50°C, however, the viscosity becomes normal. In addition specific gravity is usually below 0.85. The amount of resins plus asphaltenes is below 10%. Viscosity is generally low except when n-alkanes of high molecular weight are abundant. Aromatic content is subordinate and mostly composed of mono- and diaromatics, frequently including monoaromatic steroids. Benzothiophenes are very scarce; sulphur content is low to very low.

The paraffinic class comprises some oils from North Africa, United States, South America, some tertiary oils from West Africa, Libya, Indonesia and Central Europe.

3.4.2 Paraffinic-Naphthenic Class

The Paraffinic – Naphthenic oil is also generated in deltaic or coastal sediments of the continental margins, or in non-marine source bed, it has a moderate resins-plus –

asphaltenes content, usually 5-15% and low sulphur content (0-1%). Aromatics amount to 25-40% of the hydrocarbons. Benzo- and dibenzothiophenes are moderately abundant.

Density and viscosity are usually higher than in the paraffinic oil but remain moderate. The Paraffinic – Naphthenic class includes many crude oil from Colorado, Paris, West Texas, North Aquitaine and North Sea basins.

3.4.3 Naphthenic Class

1. There are only few crude oil in this class and this includes some immature oils from the Jurassic and Cretaceous of South America. However, the class includes mainly degraded oil which usually contains less than 20% n+isoalkanes. They originate from biochemical alteration of paraffinic or paraffinic- naphthenic oil and they usually have low sulphur content. Examples are found in the Gulf Coast area, in the North Sea, and in Russia.

3.4.4 Aromatic Intermediate

This class of crude oil is frequently generated in marine sediments, deposited in a reducing environment. They are composed of crude oil which is often heavy. Resins and asphaltenes content is about 10-30% it may sometime be higher while the sulphur content is above 1%.

Aromatics amount between 40 and 70% of hydrocarbons, the content of monoaromatics, and especially those of steroid type, is relatively low. Thiophene derivatives (benzo-and dibenzothiophene) are abundant (25-30% of the aromatics and more). The specific gravity is usually high (that is, more than 0.85). This class includes crude oil from Saudi Arabia, Quatar, Kuwait, Iraq, Syria, Turkey, some oils of West Africa,Venezuela, California, and the Mediterranean (Spain, Sicily, and Greece).

3.4.5 Aromatic-Asphaltic and Aromatic Naphthenic

These are mostly altered crude oil. During biodegradation, alkanes are first removed from crude oil. This results in shift of the crude oil away from the alkane pole. Later, a more advanced degradation may involve removal of monocycloalkanes and oxidation. Then the position of oil is also shifted toward the aromatic pole.

Therefore, most aromatic-naphthenic and aromatic-asphaltic oils are heavy, viscous oils resulting originally from degradation of paraffinic, paraffinic-naphthenic, or aromatic-intermediate oils. The resin-plus-asphaltene content is usually above 25% and may reach 60%. However, the relative content of resins and asphaltenes, and the amount of sulphur, may vary according to the type of the original crude oil.

The six classes of crude oil described above are very unevenly populated. Most normal (non-degradable) crude oil belong to three classes only. They are: aromatic-intermediate, paraffinic-naphthenic and paraffinic oil. This evaluation is based on the different oil investigated. However, if we now consider the total amount of known production and reserves, the relative importance of the classes is changed. By far the most important classes with respect to quantity are the aromatic-naphthenic, then the aromatic-asphaltic and aromatic intermediate.

Self-Assessment Exercise

1. List the most important non-hydrocarbon compounds occurring in crude oil.
2. List the various metals that we can find in crude oil.
3. What is the effect of these metals in the catalytic cracking of crude oil?
4. What are the parameters that determine the corrosiveness of crude oil?

4.0 Conclusion

This unit has examined the complex nature of crude oil mixture and the presence of some impurities that are corrosive or poisonous, as a result crude oil are not used directly as fuels or as feedstock for the production of chemicals. A general knowledge of this composite mixture is essential for establishing a processing strategy.

Crude oil is therefore, refined to separate the mixture into simpler fractions that can be used as fuels, lubricants, or as intermediate feedstock to the petrochemical industries.

5.0 Summary

In this unit, you have learnt that:

- Oil and gas form the basic sources of fuels and organic compounds in general. Fuel use takes 93% of all crude oil.
- Crude oil is almost completely made up of compounds containing carbon and hydrogen, called hydrocarbons. These include alkanes cycloalkanes and aromatic compounds.
- The complex mixture of hydrocarbons in crude oil cannot be separated easily into individual compounds by simple distillation but can however be separated into individual components by fractional distillation
- The fractions thus obtained are used as fuels and lubricants however, for the fractions to be useful as feedstock they must be chemically transformed.

6.0 Self-Assessment Exercise

1. List the various classes of crude oil. Discuss four of these classes in details.
2. Explain the following terms: (i) Ash content (ii) Pour point.
3. How would you determine Sulphur content and Salt content in crude oil?

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http//www.wikipedia.org

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Unit 2 Natural Gas Origin, Transportation and uses

1.0 Introduction

Natural Gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most useful of all energy sources. Despite its importance, however, there are many misconceptions about natural gas. Thus, in this unit, we shall discuss the historical aspect of natural gas, its formation, the various types of natural gas which includes deep natural gas, natural gas underneath the surface of the earth, tight natural gas, shale gas, coal bed gas, off shore gas, methane hydrate and other forms of gas.

2.0 Objectives

At the end of this unit, you should be able to:

- explain the formation of natural gas
- discuss the historical aspect of natural gas
- describe the natural gas under the earth
- explain briefly deep natural gas, tight natural gas, shale gas, coal bed gas and off shore gas
- explain methane hydrate
- state other forms of gas.

3.0 Main Content

3.1 **The Formation of Natural Gas**

Natural gas is a fossil fuel like oil and coal. Fossil fuels are, essentially, the remains of plants and animals and microorganisms that lived millions of years ago. So, how do these once living organisms become an inanimate mixture of gases?

There are many different theories as to the origins of fossil fuels. The most widely accepted theory says that fossil fuels are formed when organic matter (such as the remains of a plant or animal) is compressed under the earth, at very high pressure for a very long time. This is referred to as thermogenic methane. Similar to the formation of oil, thermogenic methane is formed from organic particles that are covered in mud and other sediment. Over time, more mud and sediment and other debris are piled on top of the organic matter. This sediment and debris put a great deal of pressure on the organic matter, which compresses it. This compression, combined with high temperatures found deep underneath the earth, break down the carbon bonds in the organic matter. The deeper under the earth's crust, the higher the temperature.

At low temperatures (shallower deposits), more oil is produced relative to natural gas. At higher temperatures however, more natural gas is created, as opposed to oil. That is why natural gas is usually associated with oil in deposits that are 1 to 2 miles below the earth's crust. Deeper deposits, usually contain primarily natural gas, and in many cases, pure methane.

Natural gas can also be formed through the transformation of organic matter by microorganisms. This type of methane is referred to as biogenic methane. Methanogens, methane producing microorganisms, chemically break down organic matter to produce methane. These microorganisms are commonly found in areas near the surface of the earth that are void of oxygen. These microorganisms also live in the intestines of most animals, including humans. Formation of methane in this manner usually takes place close to the surface of the earth, and the methane produced is usually lost into the atmosphere. In certain circumstances, however, this methane can be trapped underground, recoverable as natural gas. An example of biogenic methane is landfill gas. Waste containing landfills produce a relatively large amount of natural gas, from the decomposition of the waste materials that they contain. New technologies allow this gas to be harvested and added to the supply of natural gas.

Another way in which methane (and natural gas) is believed to be formed is through abiogenic processes. Extremely deep under the earth's crust, there exist hydrogen-rich gases and carbon molecules. As these gases gradually rise towards the surface of the earth, they may interact with minerals that also exist underground, in the absence of oxygen. This interaction may result in a reaction, forming elements and compounds that are found in the atmosphere (including nitrogen, oxygen, carbon dioxide, argon, and water). If these gases are under very high pressure as they move towards the surface of the earth, they are likely to form methane deposits, similar to thermogenic methane.

3.2 Natural Gas under the Earth

Although there are several ways that methane, and thus natural gas, may be formed, it is usually found underneath the surface of the earth. As natural gas has a low density, once formed it will rise towards the surface of the earth through loose, shale type rock and other material. Most of this methane will simply rise to the surface and dissipate into the atmosphere. However, a great deal of this methane will rise up into geological formations that ‘trap’ the gas under the ground. These formations are made up of layers of porous, sedimentary rock (similar to a sponge, that absorbs the gas), with a denser, impermeable layer of rock on top. This impermeable rock traps the natural gas under the ground. If these formations are large enough, they can trap a great deal of natural gas underground, in what is known as a reservoir. There are a number of different types of these formations, but the most common is created when the impermeable sedimentary rock forms a 'dome' shape, like an umbrella that catches all of the natural gas that is floating to the surface. There are a number of ways that this sort of ‘dome’ may be formed.

For instance, faults are a common location for oil and natural gas deposits to exist. A fault occurs when the normal sedimentary layers sort of 'split' vertically, so that impermeable rock shifts down to trap natural gas in the more permeable limestone or sandstone layers. Essentially, the geological formation layers of impermeable rock over more porous, oil and gas rich sediment, has the potential to form a reservoir. The picture (Fig. 1) below shows how natural gas and oil can be trapped under impermeable sedimentary rock, in what is known as an anticlinal formation.

To successfully bring these fossil fuels to the surface, a hole must be drilled through the impermeable rock to release the fossil fuels under pressure. Note that in reservoirs that contain oil and gas, the gas, being the least dense, is found closest to the surface, with the oil beneath it, typically followed by a certain amount of water.

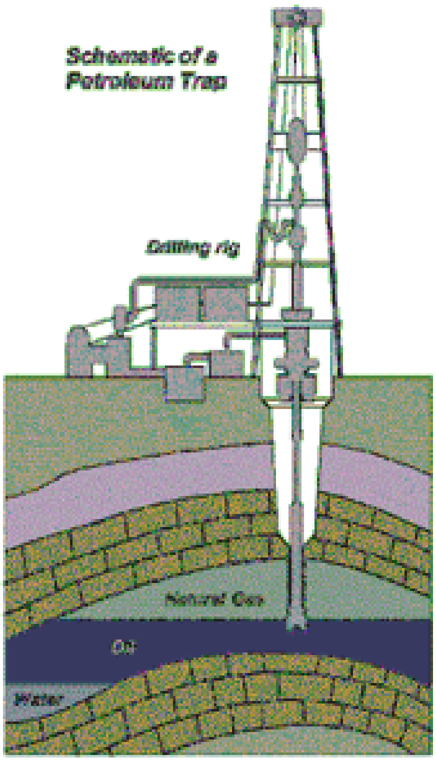

Fig. 1: Schematic Diagram of a Petroleum Trap

(Source: United State Energy Information Administration)

With natural gas trapped under the earth in this fashion, it can be recovered by drilling a hole through the impermeable rock. Gas in these reservoirs is typically under pressure, allowing it to escape from the reservoir on its own. In addition to being found in a traditional reservoir such as the one shown above, natural gas may also be found in other ‘unconventional' formations.

Historically, conventional natural gas deposits have been the most practical, and easiest, deposits to mine. However, as technology and geological knowledge advances, unconventional natural gas deposits are beginning to make up an increasingly larger per cent of the supply picture. So, what exactly is unconventional gas? A precise answer to that question is hard to find. What was unconventional yesterday, may through some technological advance, or ingenious new process, become conventional tomorrow. In the broadest sense, unconventional natural gas is gas that is more difficult, and less economically sound, to extract, usually because the technology to reach it has not been developed fully, or is too expensive.

For example, prior to 1978, natural gas that had been discovered buried deep underground in the Anadarko basin was virtually untouched. It simply wasn't economical, or possible, to extract this natural gas. It was unconventional natural gas. However, deregulation of the area (and particularly the passage of the Natural Gas Policy Act, which provided incentives towards searching and extracting unconventional natural gas), spurred investment into deep exploration and development drilling, making much of the deep gas in the basin conventionally extractable.

Therefore, what is really considered unconventional natural gas changes over time, and from deposit to deposit? The economics of extraction play a role in determining whether or not a particular deposit may be unconventional, or simply too costly to extract. Essentially, however, there are six main categories of unconventional natural gas. These are deep gas, tight gas, gas-containing shale, coal bed methane, geopressurised zones, and arctic and sub-sea hydrates.

3.3 Deep Natural Gas

Deep natural gas is exactly what it sounds like; natural gas that exists in deposits very far underground, beyond 'conventional' drilling depths. This gas is typically 15,000 feet or deeper underground, quite a bit deeper than conventional gas deposits, which are traditionally only a few thousand feet deep, at most.

Deep gas has, in recent years, become more conventional. Deep drilling, exploration, and extraction techniques have substantially improved, making drilling for deep gas economical. However, deep gas is still more expensive to produce than conventional natural gas, and as such, economic conditions have to be such that it is profitable for the industry to extract from these sources.

Self-Assessment Exercise

1. What are the misconceptions about natural gas?
2. What is pure natural gas made of?
3. What are the impurities found in natural gas?
4. What are the various ways of measuring natural gas?
5. State the most widely accepted theory of the origin of fossil fuels.

3.4 Tight Natural Gas

Another form of unconventional natural gas is referred to as tight gas. This is gas that is stuck in a very tight formation underground, trapped in unusually impermeable, hard rock, or in a sandstone or limestone formation that is unusually impermeable and non-porous (tight sand). In a conventional natural gas deposit, once drilled, the gas can usually be extracted quite readily, and easily. A great deal more effort has to be put into extracting gas from a tight formation. Several techniques exist that allow natural gas to be extracted, including fracturing and acidising. However, these techniques are also very costly. Like all unconventional natural gas, the economic incentive must be there to incite companies to extract this costly gas instead of more easily obtainable, conventional natural gas.

3.5 Shale Gas

Natural gas can also exist in shale deposits. Devonian shales are formed from the mud of shallow seas that existed about 350 million years ago (during the Devonian period of the Paleozoic era). Shale is a very fine-grained sedimentary rock, which is easily breakable into thin, parallel layers. It is a very soft rock, but does not disintegrate when it becomes wet. These shales can contain natural gas, usually when too thick, black shale deposits 'sandwich' a thinner area of shale. Because of some of the properties of these shales, the extraction of natural gas from shale formations is more difficult (and thus expensive!) than extraction of conventional natural gas. Most of the natural gas containing Devonian shale in the U.S. is located around the Appalachian Basin. Although estimates of the amount of natural gas contained in these shales are high, it is expected that only about 10% of the gas is recoverable.

However, its potential as a natural gas supply is still very promising, given an adequate technological and economic environment. As of November 2008, FERC estimated that there are 742 Tcf of technically recoverable shale gas in the United States, representing a large and growing share of total recoverable resources.

3.6 Coal Bed Methane

Coal, another fossil fuel, is formed underground under similar geologic conditions as natural gas and oil. These coal deposits are commonly found as seams that run underground, and are mined by digging into the seam and removing the coal. Many coal seams also contain natural gas, either within the seam itself or the surrounding rock. This coal bed methane is trapped underground, and is generally not released into the atmosphere until coal mining activities unleash it.

Historically, coal bed methane has been considered a nuisance in the coal mining industry. Once a mine is built, and coal is extracted, the methane contained in the seam usually leaks out into the coal mine itself. This poses a safety threat, as too high a concentration of methane in the well create dangerous conditions for coal miners. In the past, the methane that accumulated in a coal mine was intentionally vented into the atmosphere. Today, however, coal bed methane has become a popular unconventional form of natural gas. This methane can be extracted and injected into natural gas pipelines for resale, used as an industrial feedstock, or used for heating and electricity generation. The Potential Gas Committee estimates that 163.0 Tcf of technically recoverable coal bed methane exists in the United States, making up 7.8% of the total natural gas resource base. What was once a by-product of the coal industry is becoming an increasingly important source of methane and natural gas.

3.7 Geopressurised Zones

Geopressurised zones are natural underground formations that are under unusually high pressure for their depth. These areas are formed by layers of clay that are deposited and compacted very quickly on top of more porous, absorbent material such as sand or silt. Water and natural gas that is present in this clay is squeezed out by the rapid compression of the clay, and enters the more porous sand or silt deposits. This natural gas, due to the compression of the clay, is deposited in this sand or silt under very high pressure (hence the term 'geopressure').

In addition to having these properties, geopressurised zones are typically located at great depths, usually 10,000-25,000 feet below the surface of the earth. The combinations of all of these factors make the extraction of natural gas in geopressurised zones quite complicated. However, of all of the unconventional sources of natural gas, geopressurised zones are estimated to hold the greatest amount of gas. Most of the geopressurised natural gas in the U.S. is located in the Gulf Coast region. The amount of natural gas in these geopressurised zones is uncertain. However, experts estimate that anywhere from 5,000 to 49,000 Tcf of natural gas may exist in these areas! Given the current technically recoverable resources are around 1,100 Tcf, geopressurised zones offer an incredible opportunity for increasing the nation's natural gas supply.

3.8 Methane Hydrates

Methane hydrates are the most recent form of unconventional natural gas to be discovered and researched. These interesting formations are made up of a lattice of frozen water, which forms a sort of 'cage' around molecules of methane. These hydrates look like melting snow and were first discovered in permafrost regions of the Arctic. Research into methane hydrates has revealed that they may be much more plentiful than first expected. Estimates range from 7,000 Tcf to over 73,000 Tcf. In fact, the USGS estimates that methane hydrates may contain more organic carbon than the world's coal, oil, and conventional natural gas combined. However, research into methane hydrates is still in its infancy. The kind of effects the extraction of methane hydrates may have on the natural carbon cycle is not known.

Unconventional natural gas constitutes a large proportion of the natural gas that is left to be extracted in North America, and is playing an ever-increasing role in supplementing the nation's natural gas supply.

3.9 Offshore Gas Fields

Like oil, natural gas is often found underwater in offshore gas fields such as the North Sea, Corrib Gas Field off Ireland, and the Scotian Shelf near Sable Island. The technology utilised to extract and transport offshore natural gas is different from land-based fields in that a few, very large rigs are usually used, due to the cost and logistical difficulties in working over water. Rising gas prices have encouraged drillers to revisit fields that, until now, were not considered economically viable.

Fig. 2: The Drillship Discoverer Enterprise is shown in the background, at work during exploratory phase of a new offshore field. The Offshore Support Vessel Toisa Perseus is shown in the foreground, illustrating part of the complex logistics of offshore oil and gas exploration and production. *(Source: http//www.wikipedia.org)*

3.9.1 Stranded Gas Reserve

A stranded gas reserve is a natural gas field that has been discovered, but remains unusable for either physical or economic reasons. Gas that is found within oil wells is conventionally regarded as associated gas and has historically been flared. It is sometimes recirculated back into oil wells in order to maintain extraction pressure or converted into electricity using gas powered engines.

3.9.2 Economically Stranded Gas

A reserve of gas can be economically stranded for one or two reasons:

1. The reserve may be too remote from a market for natural gas, hence making the construction of pipelines prohibitively expensive.

2. The reserve may be in a region where demand for gas is saturated, and the cost of exporting gas beyond this region is too great. These are most likely to be tapped in the future when existing sources begin to run out.

3.9.3 Physically Stranded Gas

A gas field that is too deep to drill for, or is beneath an obstruction, may be considered physically stranded despite access being desirable. Continual evolution of drilling technology has progressively unlocked access to many hard fields.

3.10 Examples of Stranded Gas

Alaska has large reserves of natural gas stranded in its Prudhoe Bay oil field. The largest gas plant in the United States exists there for the sole purpose of re-injecting the associated gas back into the oil fields. Marketing of the gas awaits the completion of the Alaska gas pipeline to carry it to the lower 48 states. Building of the pipeline has been delayed by the availability of low-cost natural gas in Canada and development of non-conventional gas fields in the lower 48 states, as well as political considerations.

Canada has large amounts of stranded gas in its Arctic Islands, Beaufort Sea, and Mackenzie Delta. Marketing of this gas would require completion of the Mackenzie Valley Pipeline to bring it south along the Mackenzie River. Some companies would like to combine it with Alaska gas by building a pipeline offshore in the Arctic Ocean from Alaska to the Mackenzie Delta. The Government of Alaska is resisting this concept because it would prefer to bring the gas first to southern Alaska, and then transport it across the Yukon along the Alaska Highway.

Russia, which has the world's largest natural gas reserves, has much of it stranded in Siberia. In some cases, the easiest way to bring it to market would be to pipeline it across the Bering Strait, and then feed it into the proposed Alaska gas pipeline. Other options include moving it south to China, or west to Europe. Another option would be to build liquefied natural gas (LNG) terminals at Siberian ports, in which case it could be shipped to any port in the world with an LNG re-gasification terminal.

Self-Assessment Exercise

1. What are the forms of coal deposit?
2. What are geopressurised zones?
3. Define gas field.
4. What is the difference between conventional and unconventional gas?

4.0 Conclusion

This unit has been able to show us that natural gas is a combustible mixture of hydrocarbons gases. That natural gas is formed primarily of methane; it can also include ethane, propane, butane and pentane. Furthermore, the composition of natural gas can vary widely. Natural gas is considered dry when it is almost pure methane. It is found in reservoirs underneath the earth, natural gas is commonly associated with crude oil deposits. Production companies search for evidence of these reservoirs by using sophisticated technology that helps to find the location of the natural gas, and drill wells in the earth where it is likely to be found. Once brought from underground, the natural gas is refined to remove impurities like water, other gases, sand, and other compounds.

5.0 Summary

In this unit, you have learnt that:

- Natural gas is a fossil fuel
- Fossil fuels are formed when organic matter is compressed under the earth, at very high pressure for a very long time
- Natural gas can also be formed through the transformation of organic matter by microorganisms. This type of natural gas is referred to as biogenic methane.
- A third way in which natural gas is formed is through abiogenic processes.
- Natural gas can be divided into conventional and unconventional natural gases.
- Conventional natural gas deposits have been the most practical and easiest deposit to mine.
- Unconventional gas includes deep natural gas, tight natural gas, shale gas, coal bed gas, gas found in geopressurised zone, and methane hydrates.
- Natural gas is often found under water in offshore gas fields.
- Natural gas can be economically or physically stranded.

6.0 Self-Assessment Exercise

1. Discuss three of the various unconventional gases.
2. Define / explain the following terms: (1) Stranded gas (ii) Physically stranded gas

   (iii) Economically stranded gas.
3. What do you understand by tight natural gas?
4. List and discuss the various ways of natural gas formation.

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Unit 3 Basic Petroleum Refining

1.0 Introduction

Crude oil as it is found in nature consists of complex mixtures of compounds containing hydrogen and carbon (hydrocarbons). In addition to the hydrocarbons, compounds of sulphur, nitrogen and oxygen are present in small amounts. Furthermore, there are usually traces of vanadium, nickel, chlorine and arsenic. These compounds are harmful unless they are removed from crude oil by refining. In this unit, we shall discuss the various methods of refining crude oil. These include fractional distillation, vacuum distillation and other methods such as solvent extraction, absorption, thermal diffusion, crystallisation, absorption and stripping.

2.0 Objectives

At the end of this unit, you should be able to:

- discuss the historical aspect of refining
- describe fraction distillation of petroleum
- explain vacuum distillation
- list and explain other methods of refining crude oil.

3.0 Main Content

3.1 Historical Aspect

Petroleum refining began in the United States of America and Russia in the second half of the 19th Century, following the discovery in 1859 of “rock oil” in Pennsylvania. In the earliest refineries, simple distillation separated crude oil into impure gasoline, kerosene, lubricating oil, and fuel oil fraction. Kerosene, or lamp oil, was the principal marketable product. To improve its odour and appearance, kerosene was treated chemically with caustic soda or sulphuric acid.

The earliest automobile fuel was composed of those fractions of crude oil that were too light to be included in kerosene. Before the invention of automobile, this fraction had been virtually unstable as demand for it rose and there was increase in production and quality improvement. Methods for continuous distillation of crude oil were introduced.

After World War I a major improvement in refining came with the development of the cracking process, consisting of heating surplus heavier oils under pressure and thereby cracking, or splitting, their large molecules into the smaller ones that form the lighter, more valuable fractions. After appropriate chemical treatment, gasoline manufactured by cracking performed better in automobile engines than gasoline derived from straight distillation.

During the 1930s and World War II, sophisticated refining processes involving the use of catalysts led to further improvements in the quality of fuels and increase in supply. These improved processes, including catalytic cracking, polymerisation, alkylation, and isomerisation, permitted the petroleum industry to meet the high-performance demands of combat aircraft and, after the war, to supply the increasing quantities required by commercial aviation.

The 1950s and 1960s brought a large-scale demand for jet fuel and for high-quality lubricating oils. Catalytic reforming was established as the leading process for upgrading automotive motor gasoline for use in higher compression engines. Hydrocracking, accomplished by addition of hydrogen during refining, also improved the crude-oil fractions.

3.2 Separation into Components

The various hydrocarbon compounds that are mixed together in crude oil have different boiling points, but apart from the lightest, the differences between the boiling points of neighbouring members in the rising scale of molecular weight are so small, only fraction of a degree that they cannot be separated by ordinary distillation. Fortunately, separation is not usually necessary. Most common petroleum products consist of mixtures of compounds whose boiling points fall within a specified range.

Four main types of hydrocarbons are present in crude oil. They are normal paraffins, isoparaffins, cycloparaffins (naphthenes), and aromatics. Some crude oil, such as the heavy Mexican and Venezuelan crude oil, are predominantly naphthenic and are rich in asphalt (a high boiling semi solid material). Wax is usually, but not always, associated with paraffin-base crude oil. In addition to the hydrocarbons, compounds of sulphur, nitrogen, and oxygen are present in small amounts in crude oil. These are harmful unless they are removed. Also, there are usually traces of vanadium, nickel, chlorine and arsenic.

When a liquid mixture of compounds is heated it boils, and the vapour above the liquid is richer in the lower boiling components. If the vapour is led away from the liquid and condensed, the mixture can be separated into components boiling at different temperatures. This procedure is known as simple distillation. Chemists, working in a laboratory, normally carry out this procedure in an apparatus called distillation apparatus and it is similar to that shown in Figure 1.

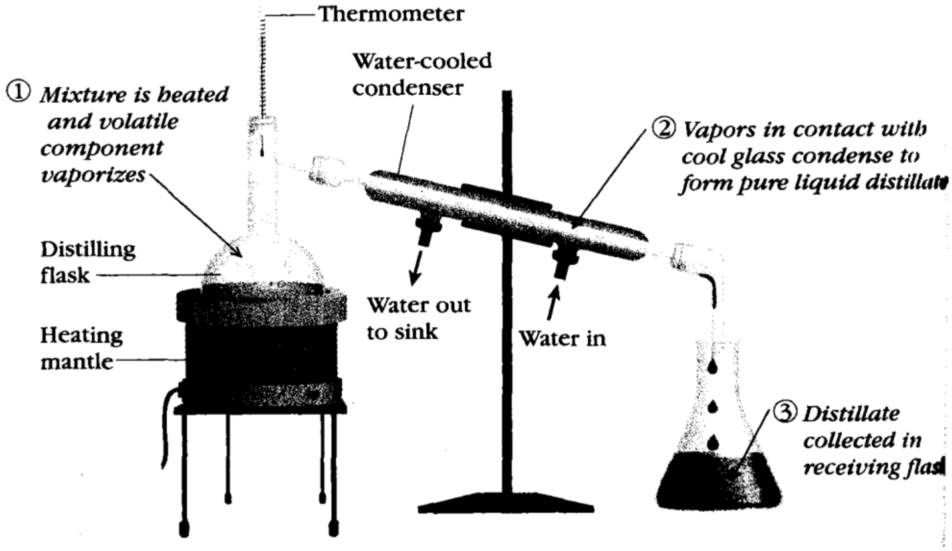

Fig. 1: A Simple Distillation Apparatus

(Source: George H. Schimd Organic Chemistry)

The temperature of the vapour condensing on the thermometer is normally taken to be the boiling temperature of any particular fraction. By changing the receiver flask when the reading on the thermometer changes, pure compounds can often be separated.

Crude oil contains so many components with similar boiling temperatures that the temperature slowly increases throughout a distillation, and as there is no clear separation, only mixtures of compounds can be obtained as a result of the fact that the boiling temperature of the constituents of crude oil are quite close to each other thus, making the isolation of individual constituents difficult.

Therefore, simple distillation is not efficient enough to separate crude oil. A related process called *fractional distillation* or *fractionation* is used. The industrial plant needed for fractionation of crude oil is very different from the laboratory equipment; though only different in scale but the principles are the same.

A schematic diagram of a fractionating tower of crude oil on industrial level is shown in Figure 2. The oil is first heated very strongly by gas burners (usually the gas used is a by-product of the fractionation). The hot, vapourised oil then passes up the tower where there is a series of trays. The higher boiling fractions collect in the lower trays and are piped out.

The lower boiling fractions pass through to higher trays before being taken off. Gases such as methane, ethane and propane are led off at the top of the tower and recycled to the burners. The boiling range of the fractions can be controlled very accurately by adjusting the amount of heating in the first stage. During fractionation the hydrocarbon are not chemically changed but are separated physically.

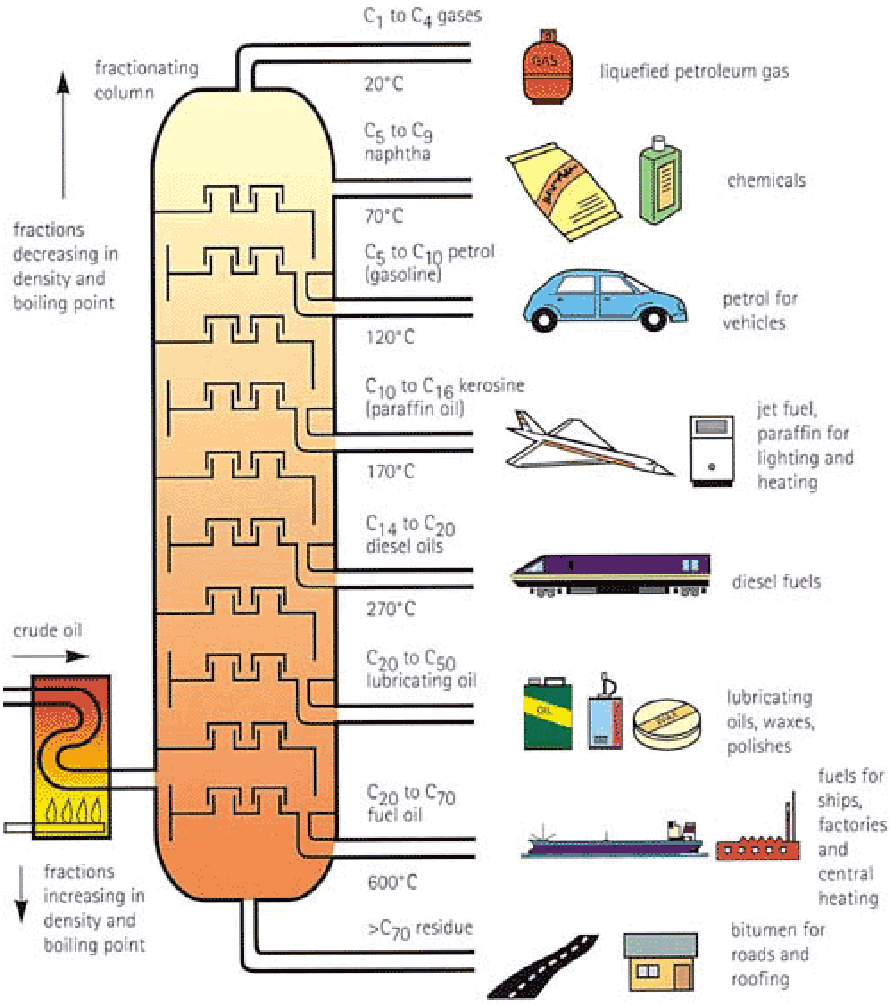

Fig. 2: Fractional Distillation Column

(Diagram by the Institute of Petroleum, UK)

The hydrocarbon fractions are, for many purposes, used unchanged. Typical uses of fractions, sometimes with other hydrocarbons added are in ascending order of boiling temperature.

The primary refinery process is fractional distillation, which may be followed by other physical separation methods, such as solvent extraction, in which superior lubricating stocks are extracted by means of a solvent, usually furfural obtained from oat hulls.

3.2.1 Fractional Distillation and Vacuum Distillation

Modern petroleum distillation units operate continuously over a long period of time and are large compared with those that carry out the same process in other industries. Units with 100,000 barrels per day capacities are common place, and units of over 200,000 barrels per day are now in operation. The American barrel is the most widely used unit in the oil industry and comprises 42 U.S. gallons, or 35 imperial gallons which is about 160 litres.

Figure 2 shows the principles of operation of a fractional distillation unit. Crude oil is pumped at a constant rate through steel alloy tubes in a furnace, fired by gas oil, and heated to a temperature between 315 and 370°C depending on the type of crude oil and the end product desired. A mixture of vapour and unvapourised oil passes from the furnace into the fractionating column, a vertical cylindrical tower as much as 150 feet (45 metres) high, provided with 30 or 40 perforated fractionating trays spaced at regular intervals. The bubble-cap tray is the commonest type used, but the sieve tray (less expensive, but with a narrower operating range) is sometimes employed. It consists of a simple perforated plate with small hole of about 3/16 to ¼ inch in diameter.

The oil vapours rise up through the column and are condensed to a liquid in a water-cooled condenser at the top. A small amount of gas remains uncondensed; this is piped away to the refinery fuel-gas system. A pressure control valve on this line maintains fractionating column pressure at the required pressure, usually near atmospheric pressure.

Part of the condensed liquid, called reflux, is pumped back into the top of the column and runs down from tray to tray, contacting the rising vapours as they pass through the slots in the bubble caps. The liquid progressively absorbs heavier constituents from the vapour and in turn loses its lighter components. Condensation and re-evaporation take place on each tray. Eventually, equilibrium is reached in which there is a continuous gradation of temperature and of oil properties throughout the column, with the lightest constituent on the top tray and the heaviest at the bottom. The use of reflux and a column of this type distinguish fractional distillation from simple distillation.

In the column shown in Figure 2, fractions called side streams are withdrawn at several points. These products have properties intermediate from the top and base of the column. Typical boiling ranges for various products are as follows; light gasoline (overhead) 25 -95°C; naphtha (no 1 side stream) 95-150°C; kerosene (no 2 side stream) 150 -230°C; and gas oil (no 3 side stream) 230-340°C.

In practice, the boiling ranges of these products can be varied within wide limits according to requirements. This is accomplished either by selecting different draw off points in the column or by varying the quantity of oil withdrawn and has the effect of changing the equilibrium concentration of the liquid on the tray concerned.

The degree of fractionation, or sharpness of separation between hydrocarbons, depends on the number of trays and their efficiency in achieving equilibrium between vapour and liquid. It also depends on the reflux ratio, i.e., the volume of liquid pumped back divided by the volume of overhead product. Reflux ratios in crude oil distillation columns are usually between 1:1 and 3:1.

Unvapourised oil entering the column (Fig. 1) flows downward over another set of trays in the lower part of column called stripping trays, which remove any light constituents remaining in the liquid. To assist in this, steam is injected at the bottom of the column. The residue that passes from the base of the fractionating column is suitable for blending into fuel oils. Alternatively, it may be distilled a second time under vacuum conditions and further quantities of distillate recovered for use as a starting material for manufacturing lubricating oil or as feedstock for catalytic cracking.

The principles of vacuum distillation resemble those of fractional distillation, and except that larger diameter columns are used to maintain comparable vapour velocities at reduced pressures, the equipment is also similar. The vacuum is produced by steam ejectors in vacuum distillation. Components that are less volatile can be distilled without raising the temperature to the range at which cracking occurs, as it would at atmospheric pressure. Firing conditions in the furnace are adjusted so that the oil temperature does not exceed about 400°C. The residue after vacuum distillation is asphalt, or bitumen.

Superfractionation is an extension of fractional distillation employing columns with a much larger number of trays (e.g. 100) and reflux ratios exceeding 5:1 with such equipment, it is possible to obtain fractions containing only a few hydrocarbons or even to separate pure compounds. By this method, isopentane of over 90% purity is produced for aviation gasoline. Isohexane and isoheptane concentrates are also prepared for the same purpose, these isoparaffins have much higher octane numbers than corresponding normal paraffins.

3.2.2 Absorption and Stripping

Absorption and stripping are processes used to obtain valuable light products such as propane / propylene and butane / butylene from the gasoline vapours that pass out of the top of the fractionating tower. In the absorption process, gasoline vapours are bubbled through absorption oil such as kerosene or heavy naphtha in equipment resembling a fractionating column. The light products dissolve in the oil while dry gases such as hydrogen, methane, ethane, and ethylene pass through undissolved. Absorption is more effective under pressure of about 100-150 pounds per square inch (7-11kg/cm) than it is at atmospheric pressure.

The light products are separated from the absorption oil in the stripping process. The solution of the absorption oil and light products is boiled by steam and passes to stripping column where the light product vapour pass upward and are recovered by condensation by water cooling under pressure. The unvapourised oil passes from the base of the column for reuse.

3.2.3 Solvent Extraction and Adsorption

Solvent extraction process is used primarily for the removal of constituents that would have an adverse effect on the performance of the product in use. The quality of kerosene is improved by the extraction of aromatic compounds that burn with a smoky flame. Another important operation is the removal of heavy aromatic compounds from lubricating oils. Removal improves viscosity-temperature relationship of the oil, extending the temperature range over which satisfactory lubrication is obtained. The usual solvents for extraction of lubricating oil are furfural and phenol. Other solvents are dichloroethylether, nitrobenzene, and a mixture of liquid propane and cresylic acid.

Certain highly porous, solid materials have the ability to select and adsorb specific types of molecules, thus separating them from other types. Silica gel is used in this way to separate aromatics from other hydrocarbons, and activated charcoal is used to remove liquid components from gases.

Adsorption is thus somewhat analogous to the process of absorption with oil, although the principles are different. Layers of the absorbed material with only a few molecules thick are formed on the extensive interior surface of the adsorbent; this interior surface may amount to several acres per pound of material.

Recent years have brought new developments in the use of adsorbents of a very selective nature called molecular sieves. Molecular sieves are produced by dehydration of naturally occurring or synthetic zeolites (crystalline alkali metal aluminosilicates). The dehydration leaves inter-crystalline cavities that have pore openings of definite size, depending upon the alkali metal of the zeolite. Under adsorptive conditions, normal paraffins molecules can enter the crystalline lattice and be selectively retained, whereas the other molecules are excluded. This principle is used commercially for the removal of normal paraffins from gasoline fuels, thus increasing their octane number. The use of molecular sieves has also been extended to the separation of hydrocarbons of higher molecular weight.

3.2.4 Thermal Diffusion and Crystallisation

When a mixture of hydrocarbons is passed through a narrow gap, of the order of 1/100 inch, between hot and cold surfaces, some of the constituents concentrate near the hot surface and others near the cold. The phenomenon is known as thermal diffusion, it is not clearly understood, but it is believed that separation occurs as a result of differences in the shapes of the molecules. Though this process has been applied in the laboratory as an analytical tool, it is unlikely to find much use in industry as the thermodynamic efficiency is low.

The crytallisation of wax from lubricating oil fractions is essential to make the oils suitable for use. A solvent, for example, a mixture of benzene and methyl ethyl ketone is first added to the oil and the solution is chilled to about 20°C. The function of the benzene is to keep the oil in solution and maintain its fluidity at low temperatures, whereas the methyl ethyl ketone (butanone) acts as a wax precipitant. Rotary filters are used to filter off the wax crystals on a specially woven canvas cloth stretched over a perforated cylindrical drum. A vacuum, maintained within the drum, sucks the oil into it. The wax crystals are removed from the cloth by metal scrapers, after washing with solvent to remove traces of oil. The solvents are later distilled from the oil and reused.

3.3 Alteration of Molecular Structure

The separation processes described above are based on differences in physical properties of the components of crude oil. By chemically changing their molecular structure, it is possible to convert less valuable hydrocarbon compound into those in demand.

The first of these conversion processes is cracking or thermal decomposition of long chain hydrocarbon molecules into shorter molecules with lower boiling points, for example, paraffin molecule such as dodecane ($C_{12}H_{26}$) has such poor antiknock properties that it cannot be used in a modern automobile engine, but under intense heat it breaks down into shorter molecules such as paraffins (C_6H_{14}) or olefins i.e. alkene (C_6H_{12}, C_5H_{10}), which are suitable for motor fuels. The chemical reactions that take place in a cracking operation are complex. The product derived from cracking process is, in effect, a synthetic crude oil.

3.4 Cracking

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are re-vapourised before cracking.

There is no any single unique reaction that happens during cracking. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds. One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:

$$C_{15}H_{32} \longrightarrow \underset{\text{ethene}}{2C_2H_4} + \underset{\text{propene}}{C_3H_6} + \underset{\text{octane}}{C_8H_{18}}$$

Or, showing more clearly what happens to the various atoms and bonds:

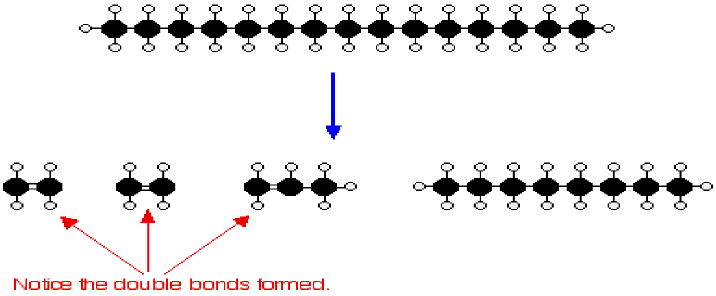

Fig. 3: Schematic Diagram of Cracking

(Source: http//www.wikipedia.org)

This is only one way in which this particular molecule might break up. The ethene and propene are important materials for making plastics or producing other organic chemicals. The octane is one of the molecules found in petrol (gasoline).

Self-Assessment Exercise

1. List the four major types of hydrocarbon found in crude oil.
2. What are the distinguishing features between simple distillation and fractional distillation?
3. Define the term cracking.
4. Why do we need to refine petroleum?

3.4.1 Thermal Cracking and Reforming

The earliest cracking techniques are typified by processes in which kerosene or gas oil materials were converted by heating to temperatures between 450-540°C at pressure of 250 to 500 pounds per square inch. This process produced gasoline with octane number 70, which is low by modern standard. In thermal cracking, high temperatures (typically in the range of 450-750°C) and pressures (up to about 70 atmospheres) are used to break the large hydrocarbons into smaller ones. Thermal cracking gives mixtures of products containing high proportions of hydrocarbons with double bonds – alkenes.

Visbreaking, another thermal cracking process, reduces viscosity of heavy crude oil residues to make them more suitable for inclusion in fuel oils.

The steam cracking process by which ethylene and other olefins are made from naphtha differs from thermal cracking in that it is carried out at low pressures and higher temperatures.

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethene (or ethylene) and propene (or propylene).

In steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG or ethane is diluted with steam and briefly heated in a furnace without the presence of oxygen. Typically, the reaction temperature is very high, at about 850°C, but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is even reduced to milliseconds, resulting in gas velocities faster than the speed of sound, to improve yield. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger.

The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time. Light hydrocarbon feeds such as ethane, LPGs or light naphtha give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil. The higher cracking temperature (also referred to as severity) favours the production of ethene and benzene, whereas lower severity produces higher amounts of propene, C4-hydrocarbons and liquid products. The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimise this. Nonetheless, a steam cracking furnace can only run for a few months at a time between de-cokings. Decoking require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

Thermal reforming, a modification of the thermal cracking process, reforms or alters the properties of low grade components such as naphthas by converting the molecules into those of higher octane number, Pressures used are somewhat higher than those in cracking.

At a temperature from 950 to 1050°F, it is possible to obtain gasoline with octane numbers of between 70 and 80 from components of less than 40.

3.4.2 Hydrocracking

Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydrotreater, the function of hydrogen is the purification of the hydrocarbon stream from sulphur and nitrogen hetero-atoms.

The products of this process are saturated hydrocarbons, depending on the reaction conditions (temperature, pressure, catalyst activity) these products range from ethane, LPG to heavier hydrocarbons comprising mostly of isoparaffins. Hydrocracking is normally facilitated by a bi-functional catalyst that is capable of rearranging and breaking hydrocarbon chains as well as adding hydrogen to aromatics and olefins to produce naphthenes and alkanes.

Major products from hydrocracking are jet fuel and diesel, while also high octane rating gasoline fractions and LPG are produced. All these products have a very low content of sulphur and other contaminants.

It is very common in India, Europe and Asia because those regions have high demand for diesel and kerosene. In the US, Fluid Catalytic Cracking is more common because the demand for gasoline is higher.

3.4.3 Catalytic Cracking

By 1950, a reforming process was introduced that employed a catalyst to improve the yield of the most desirable gasoline components while minimising the formation of unwanted heavy products and coke. (A catalyst is a substance that promotes a chemical reaction but does not take part in it.) In catalytic reforming, as in thermal reforming, a naphtha-type material serves as the feedstock, but the reactions are carried out in the presence of hydrogen, which inhibits the formation of unstable unsaturated compounds that polymerise into higher-boiling materials.

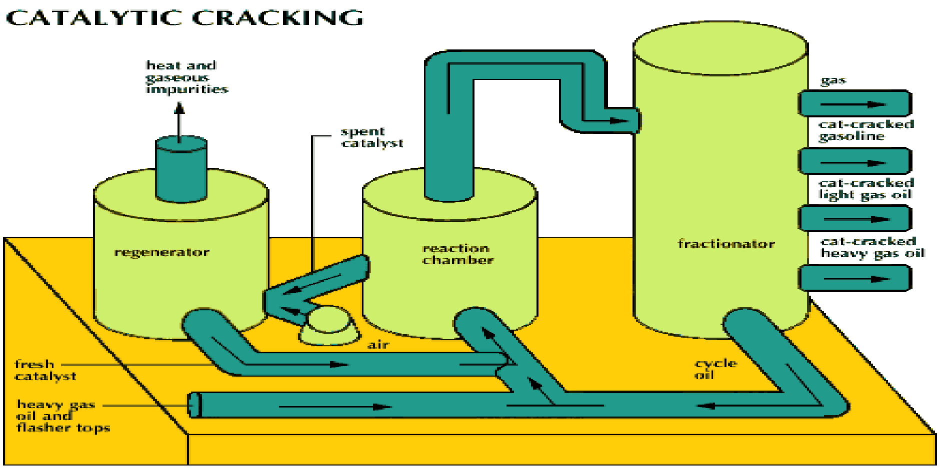

Fig. 4 A Catalytic Cracking Unit

(*Source: http//www.wikipedia.org)*

In most catalytic reforming processes, platinum is the active catalyst; it is distributed on the surface of an aluminum oxide carrier. Small amounts of rhenium, chlorine, and fluorine act as catalyst promoters. In spite of the high cost of platinum, the process is economical because of the long life of the catalyst and the high quality and yield of the products obtained. The principal reactions involve the breaking down of long-chain hydrocarbons into smaller saturated chains and the formation of isoparaffins, made up of branched-chain molecules. Formation of ring compounds (technically, the cyclisation of paraffins into naphthenes) also takes place, and the naphthenes are then dehydrogenated into aromatic compounds (ring-shaped unsaturated compounds with fewer hydrogen atoms bonded to the carbon). The hydrogen liberated in this process forms a valuable by-product of catalytic reforming. The desirable end products are isoparaffins and aromatics, both having high octane numbers.

In a typical reforming unit the naphtha charge is first passed over a catalyst bed in the presence of hydrogen to remove any sulphur impurities. The desulphurised feed is then mixed with hydrogen (about five molecules of hydrogen to one of hydrocarbon) and heated to a temperature of 500–540° C (930–1,000° F). The gaseous mixture passes downward through catalyst pellets in a series of three or more reactor vessels. Early reactors were designed to operate at about 25 kilograms per square centimetre (350 pounds per square inch), but current units frequently operate at less than 7 kg/cm^2 (100 pounds per square inch). Because heat is absorbed in reforming reactions, the mixture must be reheated in intermediate furnaces between the reactors.

After leaving the final reactor, the product is condensed to a liquid, separated from the hydrogen stream, and passed to a fractionating column, where the light hydrocarbons produced in the reactors are removed by distillation. The reformate product is then available for blending into gasoline without further treatment. The hydrogen leaving the product separator is compressed and returned to the reactor system.

Operating conditions are set to obtain the required octane level, usually between 90 and 100. At the higher octane levels, product yields are smaller, and more frequent catalyst regenerations are required. During the course of the reforming process, minute amounts of carbon are deposited on the catalyst, causing a gradual deterioration of the product yield pattern. Some units are semiregenerative facilities that is, they must be removed from service periodically (once or twice annually) to burn off the carbon and rejuvenate the catalyst system—but increased demand for high-octane fuels has also led to the development of continuous regeneration systems, which avoid the periodic unit shutdowns and maximise the yield of high-octane reformate (Fig.4). Continuous regeneration employs a moving bed of catalyst particles that is gradually withdrawn from the reactor system and passed through a regenerator vessel, where the carbon is removed and the catalyst rejuvenated for reintroduction to the reactor system.

3.5 Fluid Catalytic Cracking

Fluid Catalytic Cracking (FCC, invented by Tom Barnthouse) is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oil to more valuable gasoline, olefinic gases and other products. Cracking of petroleum hydrocarbons was originally done by thermal cracking which has been almost completely replaced by catalytic cracking because it produces more gasoline with a higher octane rating. It also produces byproduct gases that are more olefinic, and hence more valuable, than those produced by thermal cracking.

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340 °C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. This portion of crude oil is often referred to as heavy gas oil. The FCC process vapourises and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidised powdered catalyst. In effect, refineries use fluid catalytic cracking to correct the imbalance between the market demand for gasoline and the excess of heavy, high boiling range products resulting from the distillation of crude oil.

As of 2006, FCC units were in operation at 400 petroleum refineries worldwide and about one-third of the crude oil refined in those refineries is processed in an FCC to produce high-octane gasoline and fuel oils. During 2007, the FCC units in the United States processed a total of 5,300,000 barrels (834,300,000 litres) per day of feedstock and FCC units worldwide processed about twice that amount.

The modern FCC units are all continuous processes which operate 24 hours a day for as much as 2 to 3 years between shutdowns for routine maintenance. There are a number of different proprietary designs that have been developed for modern FCC units. Each design is available under a license that must be purchased from the design developer by any petroleum refining company desiring to construct and operate an FCC of a given design.

Basically, there are two different configurations for an FCC unit, the "stacked" type where the reactor and the catalyst regenerator are contained in a single vessel with the reactor above the catalyst regenerator and the "side-by-side" type where the reactor and catalyst regenerator are in two separate vessels. These are the major FCC designers and licensors. Each of the proprietary design licensors claims to have unique features and advantages.

3.5.1 Reactor and Regenerator

The schematic flow diagram of a typical modern FCC unit in Figure 5 below is based upon the "side-by-side" configuration. The preheated high-boiling petroleum feedstock (at about 315 - 430 °C) consisting of long-chain hydrocarbon molecules is combined with recycle slurry oil from the bottom of the distillation column and injected into the *catalyst riser* where it is vapourised and cracked into smaller molecules of vapour by contact and mixing with the very hot powdered catalyst from the regenerator. All of the cracking reactions take place in the catalyst riser. The hydrocarbon vapours "fluidise" the powdered catalyst and the mixture of hydrocarbon vapours and catalyst flows upward to enter the *reactor* at a temperature of about 535 °C and a pressure of about 1.72 barg.

The reactor is in fact merely a vessel in which the cracked product vapours are: (a) separated from the so-called *spent catalyst* by flowing through a set of two-stage cyclones within the reactor and (b) the *spent catalyst* flows downward through a steam stripping section to remove any hydrocarbon vapours before the *spent catalyst* returns to the *catalyst regenerator*. The flow of spent catalyst to the regenerator is regulated by a *slide valve* in the spent catalyst line.

Since the cracking reactions produce some carbonaceous material (referred to as *coke*) that deposits on the catalyst and very quickly reduces the catalyst reactivity, the catalyst is regenerated by burning off the deposited coke with air blown into the regenerator. The regenerator operates at a temperature of about 715 °C and a pressure of about 2.41 barg. The combustion of the coke is exothermic as it produces a large amount of heat that is partially absorbed by the regenerated catalyst and provides the heat required for the vapourisation of the feedstock and the endothermic cracking reactions that take place in the catalyst riser. For that reason, FCC units are often referred to as being *heat balanced*.

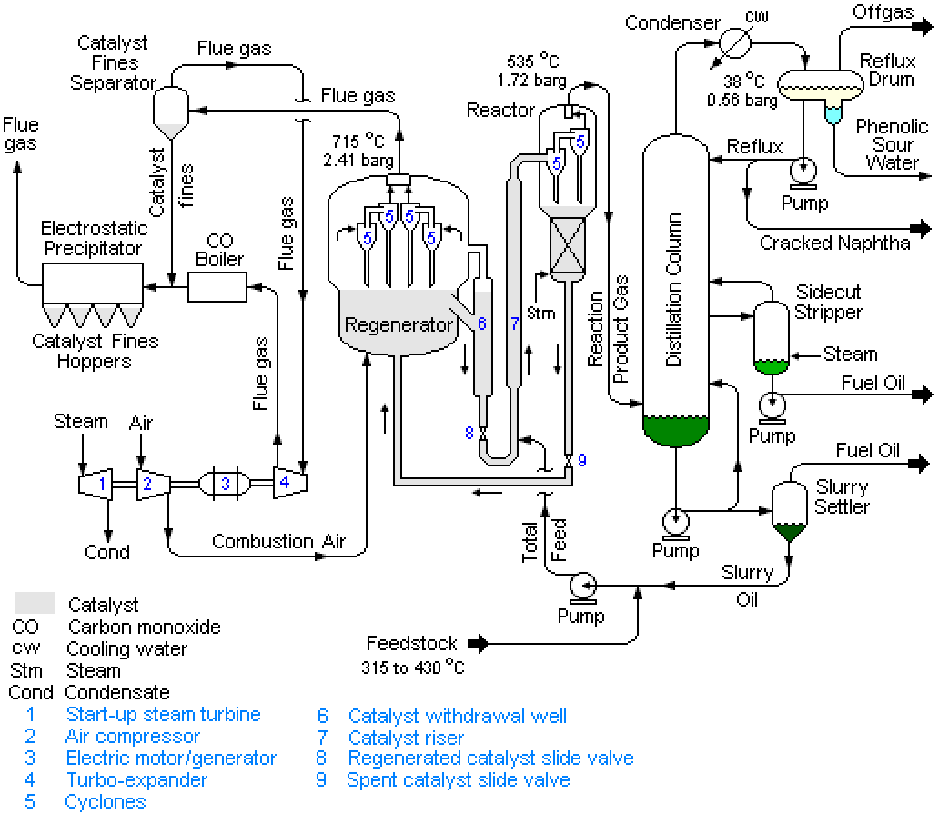

Fig. 5: A Schematic Flow Diagram of a Fluid Catalytic Cracking Unit as used in Petroleum Refineries

(Source: http//www.wikipedia.org)

The hot catalyst (at about 715 °C) leaving the regenerator flows into a *catalyst withdrawal well* where any entrained combustion flue gases are allowed to escape and flow back into the upper part to the regenerator. The flow of regenerated catalyst to the feedstock injection point below the catalyst riser is regulated by a slide valve in the regenerated catalyst line. The hot flue gas exits in the regenerator after passing through multiple sets of two-stage cyclones that remove entrained catalyst from the flue gas.

The amount of catalyst circulating between the regenerator and the reactor amounts to about **5 kg per kg of feedstock** which is equivalent to about 4.66 kg per litre of feedstock. Thus, an FCC unit processing 75,000 barrels/day (12,000,000 litres/day) will circulate about 55,900 metric tons per day of catalyst.

3.5.2 Distillation Column

The reaction product vapours (at 535 °C and a pressure of 1.72 barg) flow from the top of the reactor to the bottom section of the distillation column (commonly referred to as the *main fractionator*) where they are distilled into the FCC end products of cracked naphtha, fuel oil and offgas.

After further processing for removal of sulphur compounds, the cracked naphtha becomes a high-octane component of the refinery's blended gasolines.

The main fractionator off gas is sent to what is called a *gas recovery unit* where it is separated into butanes and butylenes, propane and propylene, and lower molecular weight gases (hydrogen, methane, ethylene and ethane). Some FCC gas recovery units may also separate out some of the ethane and ethylene.

Although the schematic flow diagram (Fig. 5) overleaf depicts the main fractionator as having only one side cut stripper and one fuel oil product, many FCC main fractionators have two strippers and produce a light fuel oil and a heavy fuel oil. Likewise, many FCC main fractionators produce light cracked naphtha and a heavy cracked naphtha. The terminology *light* and *heavy* in this context refers to the product boiling ranges, with light products having a lower boiling range than heavy products.

The bottom product oil from the main fractionator contains residual catalyst particles which were not completely removed by the cyclones in the top of the reactor. For that reason, the bottom product oil is referred to as slurry *oil*. Part of that slurry oil is recycled back into the main fractionator above the entry point of the hot reaction product vapours so as to cool and partially condense the reaction product vapours as they enter the main fractionator. The remainder of the slurry oil is pumped through a slurry settler. The bottom oil from the slurry settler contains most of the slurry oil catalyst particles and is recycled back into the catalyst riser by combining it with the FCC feedstock oil. The so-called *clarified slurry oil* or decant oil is withdrawn from the top of slurry settler for use elsewhere in the refinery or as a heavy fuel oil blending component.

3.5.3 Regenerator Flue Gas

Depending on the choice of FCC design, the combustion in the regenerator of the coke on the spent catalyst may or may not be complete combustion to carbon dioxide (CO_2). The combustion air flow is controlled so as to provide the desired ratio of carbon monoxide (CO) to carbon dioxide (CO_2) for each specific FCC design.

In the design shown in Figure 5, the coke has only been partially combusted to CO_2. The combustion flue gas (containing CO and CO_2) at 715 °C and at a pressure of 2.41 barg is routed through a secondary catalyst separator containing *swirl tubes* designed to remove 70 to 90% of the particulates in the flue gas leaving the regenerator. This is required to prevent erosion damage to the blades in the turbo-expander that the flue gas is next routed through.

The expansion of flue gas through a turbo-expander provides sufficient power to drive the regenerator's combustion air compressor. The electrical motor-generator can consume or produce electrical power. If the expansion of the flue gas does not provide enough power to drive the air compressor, the electric motor/generator provides the needed additional power. If the flue gas expansion provides more power than needed to drive the air compressor, than the electric motor/generator converts the excess power into electric power and exports it to the refinery's electrical system.

The expanded flue gas is then routed through a steam-generating boiler (referred to as a *CO boiler*) where the carbon monoxide in the flue gas is burned as fuel to provide steam for use in the refinery as well as to comply with any applicable environmental regulatory limits on carbon monoxide emissions.

The flue gas is finally processed through an electrostatic precipitator (ESP) to remove residual particulate matter to comply with any applicable environmental regulations regarding particulate emissions. The ESP removes particulates in the size range of 2 to 20 microns from the flue gas.

The steam turbine in the flue gas processing system (shown in the above diagram) is used to drive the regenerator's combustion air compressor during start-ups of the FCC unit until there is sufficient combustion flue gas to take over that task.

3.5.4 Catalysts

Modern FCC catalysts are fine powders with a bulk density of 0.80 to 0.96 g/cc and having a particle size distribution ranging from 10 to 150 **µm** and an average particle size of 60 to 100 **µm**. The design and operation of an FCC unit is largely dependent upon the chemical and physical properties of the catalyst. The desirable properties of an FCC catalyst are:

- Good stability to high temperature and to steam
- High activity
- Large pore sizes
- Good resistance to attrition
- Low coke production

A modern FCC catalyst has four major components: crystalline zeolite, matrix, binder and filler. Zeolite is the primary active component and can range from about 15 to 50 weight percent of the catalyst. The zeolite used in FCC catalysts is referred to as faujasite or as Type Y and is comprised of silica and alumina tetrahedra with each tetrahedron having either an aluminium or a silicon atom at the center and four oxygen atoms at the corners. It is a molecular sieve with a distinctive lattice structure that allows only a certain size range of hydrocarbon molecules to enter the lattice. In general, the zeolite does not allow molecules larger than 8 to 10 nm (i.e., 80 to 90 angstroms) to enter the lattice.

The catalytic sites in the zeolite are strong acids (equivalent to 90% sulphuric acid) and provide most of the catalytic activity. The acidic sites are provided by the alumina tetrahedra. The aluminum atom at the center of each alumina tetrahedra is at a **+3** oxidation state surrounded by four oxygen atoms at the corners which are shared by the neighbouring tetrahedra. Thus, the net charge of the alumina tetrahedra is **-1** which is balanced by a sodium ion during the production of the catalyst. The sodium ion is later replaced by an ammonium ion which is vapourised when the catalyst is subsequently dried, resulting in the formation of Lewis and Brønsted acidic sites. In some FCC catalysts, the Brønsted sites may be later replaced by rare earth metals such as cerium and lanthanum to provide alternative activity and stability levels.

The matrix component of an FCC catalyst contains amorphous alumina which also provides catalytic activity sites and in larger pores that allows entry for larger molecules than does the zeolite. That enables the cracking of higher-boiling, larger feedstock molecules than are cracked by the zeolite.

The binder and filler components provide the physical strength and integrity of the catalyst. The binder is usually silica sol and the filler is usually clay (kaolin). Nickel, vanadium, iron, copper and other metal contaminants, present in FCC feedstock in the parts per million ranges, all have detrimental effects on the catalyst activity and performance.

Nickel and Vanadium are particularly troublesome. There are a number of methods for mitigating the effects of the contaminant metals listed as follows:

- Avoid feedstock with high metals content: This seriously hampers a refinery’s flexibility to process various crude oil or purchased FCC feedstocks.

- Feedstock feed pretreatment: Hydro-desulphurisation of the FCC feedstock removes some of the metals and also reduces the sulphur content of the FCC products. However, this is a costly option.

- Increasing fresh catalyst addition: All FCC units withdraw some of the circulating equilibrium catalyst as spent catalyst and replace it with fresh catalyst in order to maintain a desired level of activity. Increasing the rate of such exchange lowers the level of metals in the circulating equilibrium catalyst, but this is also a costly option.

- Demetalisation: The commercial proprietary Demet Process removes nickel and vanadium from the withdrawn spent catalyst. The nickel and vanadium are converted to chlorides which are then washed out of the catalyst. After drying, the demetalised catalyst is recycled into the circulating catalyst. Removals of about 95% nickel and 67 to 85% vanadium have been reported. Despite that, the use of the Demet process has not become widespread, perhaps because of the high capital expenditure required.

Metals passivation: Certain materials can be used as additives which can be impregnated into the catalyst or added to the FCC feedstock in the form of metal-organic compounds. Such materials react with the metal contaminants and passivate the contaminants by forming less harmful compounds that remain on the catalyst. For example, antimony and bismuth are effective in passivating nickel and tin is effective in passivating vanadium. A number of proprietary passivation processes are available and fairly widely used.

Self-Assessment Exercise

1. Define or explain the following terms: (i) Visbreaking (ii) Steam cracking (iii) Thermal reforming

2. What are the desirable properties of an FCC catalyst?

3. There are two different configurations for an FCC unit.

4. Why is the bottom product oil from the main fractionators of a distillation column called slurry oil.

4.0 Conclusion

In this unit, you have learnt that petroleum is a complex mixture of compounds containing hydrogen and carbon. In addition, compounds of sulphur, nitrogen and oxygen are present in small amounts; furthermore, there are usually traces of vanadium, nickel, chlorine and arsenic. As a result of the harmful nature of these compounds there is a need to remove them from crude oil by refining. You have also been able to learn the various methods of refining crude petroleum which include fractional distillation, vacuum distillation, absorption, stripping, solvent extraction, adsorption, thermal diffusion and crystallisation. Other methods are thermal cracking and reforming, hydrocracking, catalytic cracking, and fluid catalytic cracking.

5.0 Summary

In this unit, you have learnt that:

- Petroleum refining began in the United States of America and Russia in the second half of the 19th Century, following the discovery in 1859 of "rock oil" in Pennsylvania.

- Crude oil is a complex mixture of compounds containing hydrocarbons. In addition to the hydrocarbons, compounds of sulphur, nitrogen and oxygen are present in small amounts furthermore, there are usually traces of vanadium, nickel, chlorine and arsenic. These compounds are harmful unless removed from crude oil by refining.

- Fractional distillation, vacuum distillation, absorption, stripping, solvent extraction, adsorption, thermal diffusion and crystallisation are some of the methods used in refining crude petroleum.

- The processes mentioned in 3 above are based on differences in physical properties of the components of crude oil however, by chemically changing the molecular structure of the various components of crude oil, it is possible to convert less valuable hydrocarbon compound into valuable one. This is known as alteration of molecular structure.

- Thermal cracking and reforming, hydrocracking, catalytic cracking, and fluid catalytic cracking are some of the methods used in alteration of molecular structure.

6.0 Self-Assessment Exercise

1. What are the desirable properties of a fluid catalytic cracking catalyst?

2. List the major components of a modern fluid catalytic cracking catalyst

3. Write short note on each of the components of a modern fluid catalytic cracking catalyst.

4. What do you understand by the term feedstock?

5. List the various methods of altering molecular structure in crude petroleum.

6. What is the primary reason for carrying out solvent extraction in crude petroleum?

7. What are the various methods of mitigating the effects of the contaminant metals in fluid catalytic cracking catalyst?

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Unit 4 Natural Gas Treatment Processes

1.0 Introduction

Like crude oil, natural gas is also found in complex mixture with other gases such as carbon dioxide, hydrogen sulphide, and water vapour, the presence of these gases is undesirable, for instance the presence of hydrogen sulphide in natural gas is poisonous, more importantly if the gas is for domestic use. In this unit we are going to look at the various ways of making natural gas safe and of great heating value.

2.0 Objectives

At the end of this unit, you should be able to:

- explain the treatment of acid gas
- describe the condensable gas hydrocarbons
- explain the process of treatment of liquefied natural gas
- state the properties of natural gas.

3.0 Main Content

3.1 Natural Gas Treatment Processes

Raw natural gases contain variable amounts of carbon dioxide, hydrogen sulphide, and water vapour. The presence of hydrogen sulphide 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 vapour reduced. In addition, natural gas with appreciable amounts of heavy hydrocarbons should be treated for their recovery as natural gas liquids.

3.2 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.

3.2.1 Physical Absorption

Selexol, sulphinol, and rectisol are the most important processes used for physical absorption of gases. In addition, they are also commercially viable. 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. In the

Selexol process for example, the solvent is dimethyl ether of polyethylene glycol. Raw natural gas passes counter currently to the descending solvent. When the solvent becomes saturated with the acid gases, the pressure is reduced, and hydrogen sulphide and carbon dioxide are desorbed. The solvent is then recycled to the absorption tower. Figure 1 shows the Selexol process.

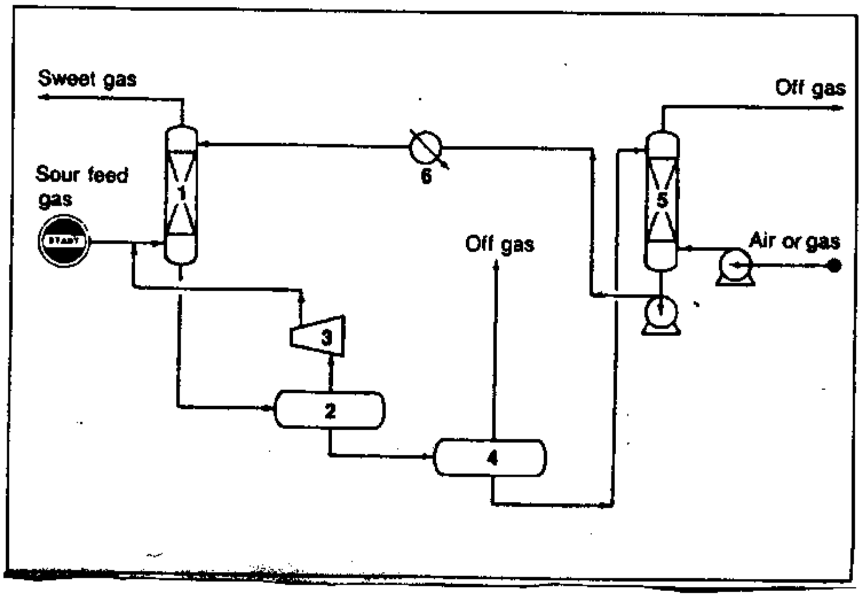

Fig. 1: The Selexol Process for Acid Gas Removal: (1) Absorber, (2) Flash Drum, (3) Compressor, (4) Low-pressure Drum, (5) Stripper, (6) Coole

(Source: Chemistry of Petrochemical Processes)

3.2.2 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 sulphide and carbon disulphide are low. Molecular sieves are also capable of adsorbing water in addition to the acid gases.

Self-Assessment Exercise

1. What are the disadvantages of having the following gases in natural gas?

(a) Hydrogen sulphide (H_2S)
(b) Carbon dioxide (CO_2)
2. What are the various ways of removing acid gas from natural gas?

3.2.3 Chemical Absorption (Chemisorption)

This processes is characterised by a high capability of absorbing large amounts of acid gases. A solution of a relatively weak base, such as monoethanolamine is used. 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 sulphides, carbonates, and bicarbonates are formed. Diethanolamine is a favoured 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 sulphides (COS), while the monoethanotamine reacts irreversibly with 95% of the COS and forms a degradation product that must be disposed of. Diglycolamine (DGA), is another amine solvent used in the econamine process (Fig. 2). Absorption of acid gases occurs in an absorber containing an aqueous solution of DGA, and the heated rich solution (saturated with acid gases) is pumped to the regenerator. Diglycolamine solutions are characterised 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 from stable salts, which are not easily regenerated. For example, carbon dioxide and hydrogen sulphide react with aqueous sodium hydroxide to yield sodium carbonate and sodium sulphide, respectively.

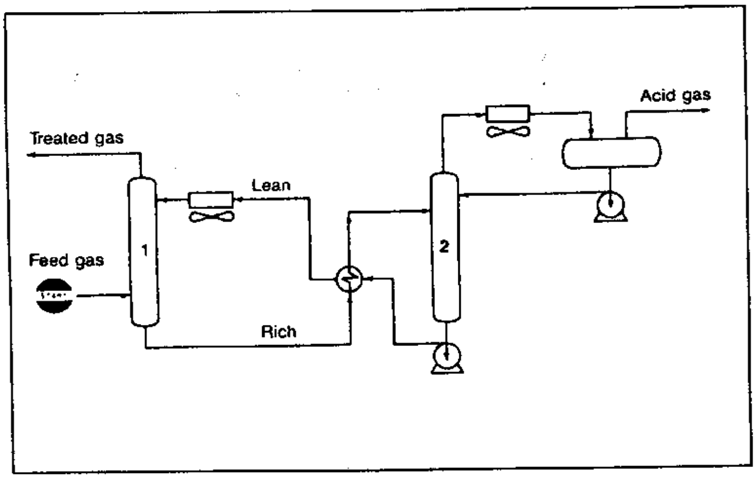

Fig. 2: The Econamine Process: (1) Absorption Tower, (2) Regeneration Tower

(Source: Chemistry of Petrochemical Processes)

$$CO_2 + 2NaOH_{(aq)} \longrightarrow Na_2CO_3 + H_2O$$

$$H_2S + 2\ NaOH_{(aq)} \longrightarrow Na_2S + 2\ H_2O$$

However, a strong caustic solution is used to remove mercaptans from gas and liquid streams. In the Merox Process, for example, a caustic solvent containing a catalyst such as cobalt, which is capable of converting mercaptans (RSH) to caustic insoluble disulphides (RSSR), is used for streams rich in mercaptans after removal of H_2S. Air is used to oxidise the mercaptans to disulphides. The caustic solution is then recycled for regeneration. The

Merox process (Fig. 3) is mainly used for treatment of refinery gas streams. In general, primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered. Natural gas and crude oil are the basic raw materials for the manufacture of petrochemicals.

Secondary raw materials, or intermediates, are obtained from natural gas and crude oil through different processing schemes. The intermediates may be light hydrocarbon compounds such as methane and ethane, or heavier hydrocarbon 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 oil (Substitute Natural Gas (SNG) and synthetic crudes from coal, tar sand and oil shale).

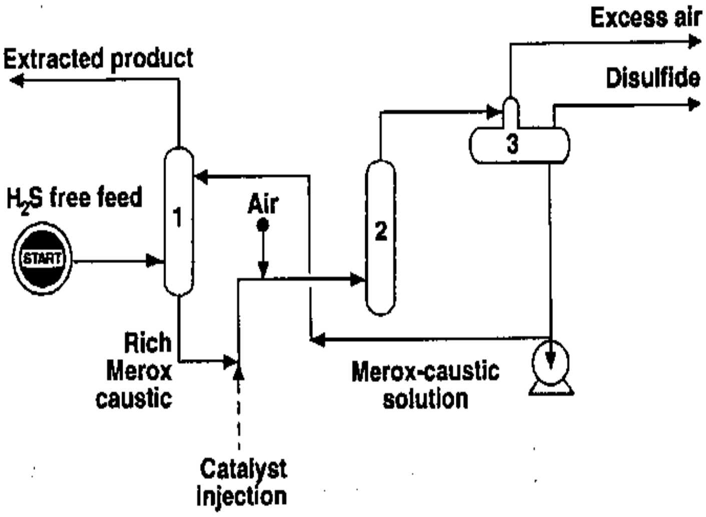

Fig. 3: The Merox Process: (1) Extractor, (2) Oxidation Reactor

(Source: Chemistry of Petrochemical Processes)

3.2.4 Water Removal

Moisture must be removed from natural gas to reduce corrosion problems and to prevent hydrate formation. Hydrates 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 vapour phase processes because of its low vapour 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 vapour-liquid equilibrium data. Predicting the interaction between TEG and water vapour in natural gas over a broad range allows the designs for ultra-low dew point applications to be made. A computer program was developed by

Grandhidsan *et al.* (1999), to estimate the number of trays and the circulation rate of lean TEG needed to dry natural gas. It was found that more accurate predictions of the rate could be achieved using this program than using hand calculation.

Figure 4 shows the Dehydrate process where EG, DEG or TEG could be used as an absorbent. One alternative to using bubble-cap trays is structural packing, which improves control of mass transfer. Flow passages direct the gas and liquid flow countercurrent to each other. 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.

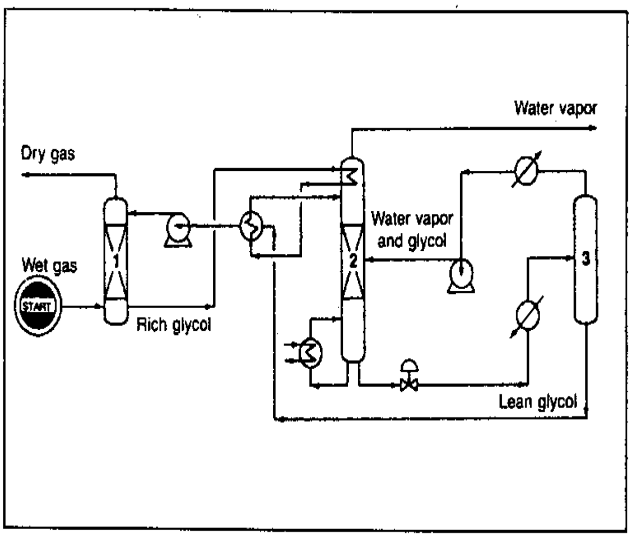

Fig. 4: Flow Diagram of the Dehydrate Process: (1) Absorption Column,

(2) Glycol Sill, (3) Vacuum Drum

(Source: Chemistry of Petrochemical Processes)

3.3 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 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 (–15 to –180°F), which are achieved primarily through adiabatic expansion of the inlet gas.

Table 1: Components of a Typical Natural Gas before and after Treatment

Pipeline Gas	Feed	Components Mole (%)
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	0.006	0.004
C64	0.11	0.014

(Source: Chemistry of Petrochemical Processes)

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 demethaniser to separate methane from NGL. Improved NGL recovery could be achieved through better control strategies and use of on-line gas chromatographic analysis.

3.4 Natural Gas Liquid (NGL)

Natural gas liquids (condensable hydrocarbons) are those hydrocarbons heavier than methane that is 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) consists of $C5^+$ hydrocarbons and is added to gasoline to raise its vapour pressure. Natural gasoline is usually sold according to its vapour pressure.

Natural gas liquids may contain significant amounts of cyclohexane, a precursor for nylon 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 by Phillips Petroleum Company to separate cyclohexane.

3.5 Liquefied Natural Gas (LNG)

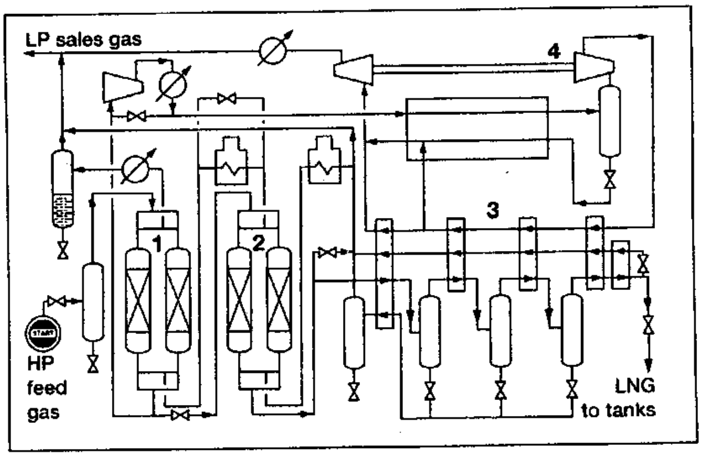

Fig. 5: Flow Diagram of the Expander Cycle for Liquefying Natural Gas:

(1) Pretreatment (mol.sieve), (2) Heat Exchanger, (3) Turboexpander

(Source: Chemistry of Petrochemical Processes)

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 vapour below 10 ppm and carbon dioxide and hydrogen sulphide 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. Through 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. Figure 5 is a flow diagram for the expander cycle for liquefying natural gas. In mechanical refrigeration, a multicomponent refrigerant consisting of nitrogen, methane, ethane, and propane is used through a cascade cycle. When these liquids evapourate, the heat required is obtained from natural gas, which loses energy/temperature till it is liquefied. The refrigerant gases are recompressed and recycled. Figure 6 shows the MCR natural gas liquefaction process. Table 2 lists important properties of a representative liquefied natural gas mixture.

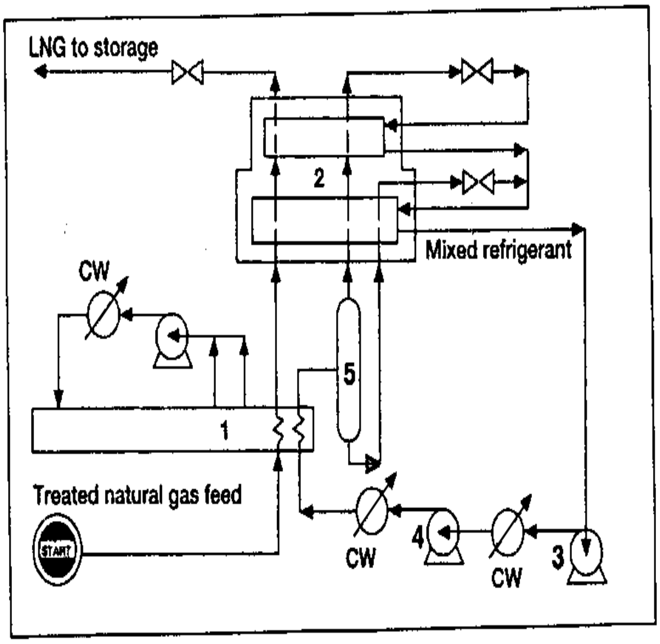

Fig. 6: The MCR Process for Liquefying Natural Gas: (1) Coolers, (2) Heat Exchangers, (3,4) Two Stage Compressors, (5) Liquid-Vapour Phase Separator

(Source: Chemistry of Petrochemical Processes)

3.6 Properties of Natural Gas

Treated natural gas consists mainly of methane; the properties of both gases (natural gas and methane) are nearly similar. However, natural gas is not pure methane, and its properties are modified by the presence of impurities, such as N_2 and CO_2 and small amounts of unrecovered heavier hydrocarbons.

Table 2: 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.

(Source: Chemistry of Petrochemical Processes)

An important property of natural gas is its heating value. Relatively high amounts of nitrogen and/or carbon dioxide reduce the heating value of the gas. Pure methane has a heating value of 1,009 Btu/ft^3. This value is reduced to approximately 900 Btu/ft^3 if the gas contains about 10% N_2 and CO_2. (The heating value of either nitrogen or carbon dioxide is zero.) On the other hand, the heating value of natural gas could exceed methane's due to the presence of higher-molecular weight hydrocarbons, which have higher heating values. For example, ethane's heating value is 1,800 Btu/ft^3, compared to 1,009 Btu/ft^3 for methane. Heating values of hydrocarbons normally present in natural gas are shown in a Table. Natural gas is usually sold according to its heating values. The heating value of a product gas is a function of the constituents present in the mixture. In the natural gas trade, a heating value of one million Btu is approximately equivalent to 1,000 ft^3 of natural gas.

3.7 Gas Hydrates

Gas hydrates are ice-like materials which consist of methane molecules encaged in a cluster of water molecules and held together by hydrogen bonds. This material occurs in large underground deposits found beneath the ocean floor on continental margins and in places north of the Arctic Circle such as Siberia. It is estimated that gas hydrate deposits contain twice as much carbon as all other fossil fuels on earth. This source, if proven feasible for recovery, could be a future energy as well as chemical source for petrochemicals.

Due to its physical nature (a solid material only under high pressure and low temperature), it cannot be processed by conventional methods used for natural gas and crude oil. One approach is by dissociating this cluster into methane and water by injecting a warmer fluid such as sea water. Another approach is by drilling into the deposit. This reduces the pressure and frees methane from water. However, the environmental effects of such drilling must still be evaluated.

Self-Assessment Exercise

1. What is the name of the base that is normally used in chemical absorption?
2. Name the two methods used to liquefy natural gas
3. Why must moisture be removed from natural gas
4. Explain the following terms: (i) NGL (ii) LNG

4.0 Conclusion

In this unit, you have learnt the various methods of treating raw natural gas, because the presence of impurities such as carbon dioxide, hydrogen sulphide, and water vapour are undesirable. The various method of treating raw natural gas was also discussed. In addition, properties of treated natural gas was discussed, although, treated natural gas consists mainly of methane however, natural gas is not pure methane. The properties of treated natural gas were compared with pure methane.

5.0 Summary

In this unit, you have learnt that:

- Raw natural gas is found as a complex mixture with other gases such as carbon dioxide, hydrogen sulphide, and water vapour.

- The presence of these gases is undesirable, for instance the presence of hydrogen sulphide in natural gas is poisonous more importantly if the gas is for domestic use.
- Raw natural gas can be treated by various methods and these include: physical absorption, physical adsorption, chemical absorption, and water removal.
- Hydrocarbons heavier than methane (condensable hydrocarbon) are valuable raw material and important fuel.
- Hydrocarbons heavier than methane are known as natural gas liquids (NGL).
- The amount of NGL recover from raw natural gas depends mainly on the percentage of the heavier hydrocarbons present in the gas and on the efficiency of the process used to recover them.
- Gas hydrates are ice-like materials which consist of methane molecules encaged in a cluster of water molecules held together by hydrogen bonds.

6.0 Self-Assessment Exercise

1. Acid gases can be reduced or removed by one or more methods. Discuss all the methods.
2. List and discuss the three streams that natural gas liquids are fractionated into.
3. How can hydrocarbon heavier than methane be recovered using lean oil extraction?
4. How and why is water vapour removed from raw natural gas

7.0 Reference/Further Reading

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