NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLGY

COURSE CODE: CHM311

COURSE TITLE: PETROLEUM CHEMISTRY

COURSE GUIDE

CHM311
PETROLEUM CHEMISTRY

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Introduction

Introduction to Petroleum Chemistry is a second semester course. It is a two-unit credit degree course available to all students offering the Bachelor of Science (B.Sc.) Chemistry.

Petroleum Chemistry is a special field of general chemistry. The practitioner is primarily a chemist and must be trained in the same way and work with the same method as his/her colleagues who specialise in other areas of chemistry. If we are to follow this, it is not possible to discuss the development of petroleum chemistry without treating the development of general chemistry simultaneously.

The concept of Petroleum Chemistry has various meanings to people in different fields. The main concern of Petroleum Chemistry is with the petroleum engineers, with petroleum occupation, and with problems associated with petroleum production. Petroleum Chemistry is a discipline which studies the various problems associated with petroleum production. The purpose underlying the study of Petroleum Chemistry is to develop greater and better ways of solving associated problems with production of petroleum products.

What you will Learn in this Course

The course consists of units and a Course Guide. This Course Guide tells you briefly what the course is about, what course materials you will be using and how you can work with these materials. In addition, it advocates some general guidelines for the amount of time you are likely to spend on each unit of the course in order to complete it successfully.

It gives you guidance in respect of your Tutor-Marked Assignment which will be made available in the assignment file. There will be regular tutorial classes that are related to the course. It is advisable for you to attend these tutorial sessions. The course will prepare you for the challenges you will meet in the field of Petroleum Chemistry.

Course Aims

The aim of the course is not complex. The course aims to provide you with an understanding of Petroleum Chemistry; it also aims to provide you with solutions to problems in Petroleum Chemistry.

Course Objectives

To achieve the aims set out, the course has a set of objectives. Each unit has specific objectives which are included at the beginning of the unit.

You should read these objectives before you study the unit. You may wish to refer to them during your study to check on your progress. You should always look at the unit objectives after completion of each unit. By doing so, you would have followed the instructions in the unit.

Below are the comprehensive objectives of the course as a whole. By meeting these objectives, you should have achieved the aims of the course as a whole. In addition to the aims above, this course sets to achieve some objectives. Thus, after going through the course, you should be able to:

explain the concept of Petroleum Chemistry and its significance
identify the basic concepts, terms and important events in the development of Petroleum Chemistry.
identify the significance, strategies, approaches and problems in Petroleum Chemistry

Course Materials

The main components of the course are:

1. The Course Guide
2. Study Units
3. References/Further Reading
4. Assignments
5. Presentation Schedule

Study Units

The study units in this course are as follows:

Module 1	**Basic Concepts in Petroleum Chemistry**
Unit 1	Origin of Crude Oil
Unit 2	Fate of Organic Matter in Sedimentary Basins
Unit 3	Gas Origin, Transportation and Uses
Unit 4	Oil Well, Oil Field and Reservoir

Module 2	**Composition of Crude and Natural Gas**
Unit 1	Composition, Properties and Classification of Crude oil
Unit 2	Origin, Transportation and Uses
Unit 3	Basic Petroleum Refining
Unit 4	Natural Gas Treatment Processes

Module 3 Distribution of Petroleum and Natural Gases Resources

Unit 1 Distribution of Natural Gases
Unit 2 Nigeria Natural Gas Potential
Unit 3 Petrochemicals from Natural Gas

The first unit of module one focuses on the basic concept in Petroleum Chemistry *viz-a-viz* the origin of petroleum. The second unit deals with the fate of organic matter in sedimentary basins. The third and the fourth units are concerned with the origin of natural gas, its transportation and the various types of oil and gas well, oil fields and reservoir.

Units one, two, three and four of module two deal with the composition, properties and classification of crude oil and natural gases, refining and treatment of natural gas.

While, units one, two and three of module three are concerned with distribution of petroleum, distribution of natural gases, Nigeria natural gas potential and petrochemicals from natural gas.

Each unit consists of one or two weeks' work and includes an introduction, objectives, reading materials, exercises, conclusion, summary, tutor-marked assignments (TMAs) and references/further reading. The unit directs you to work on exercises related to the required reading. In general, these exercises test you on the materials you have just covered or require you to apply it in some way and thereby assist you to evaluate your progress and to reinforce your comprehension of the material. Together with TMAs, these exercises will help you in achieving the stated learning objectives of the individual units and of the course as a whole.

Presentation Schedule

Your course materials have important dates for the early and timely completion and submission of your TMAs and attending tutorials. You should remember that you are required to submit all your assignments by the stipulated time and date. You should guard against falling behind in your work.

Assessment

There are three aspects to the assessment of the course. First is made up of Self Assessment Exercises, second consists of the Tutor-Marked Assignments and third is the written examination/end of course examination.

You are advised to do the exercises. In tackling the assignments, you are expected to apply information, knowledge and techniques you gathered during the course. The assignments must be submitted to your facilitator for formal assessment in accordance with the deadlines stated in the presentation schedule and the assignment file. The work you submit to your tutor for assessment will count for 30% of your total course mark. At the end of the course you will need to sit for a final or end of course examination of about three hours duration. This examination will count for 70% of your total course mark.

Tutor-Marked Assignments (TMAs)

The TMA is a continuous assessment component of your course. It accounts for 30% of the total score. You will be given four (4) TMAs to answer. Three of these must be answered before you are allowed to sit for the end of the course examination. The TMAs would be given to you by your facilitator and returned after you have done the assignment. Assignment questions for the units in this course are contained in the assignment file. You will be able to complete your assignment from the information and material contained in your reading, references and study units. However, it is desirable in all degree levels of education to demonstrate that you have read and researched more into your references, which will give you a wider view point and may provide you with a deeper understanding of the subject.

Make sure that each assignment reaches your facilitator on or before the deadline given in the presentation schedule and assignment file. If for any reason you cannot complete your work on time, contact your facilitator before the assignment is due to discuss the possibility of an extension. Extension will not be granted after the due date unless in exceptional circumstances.

Final Examination and Grading

The end of course examination for introduction to Petroleum Chemistry will be for about two hours and it has a value of 70% of the total course score. The examination will consist of questions, which will reflect the type of self-testing, practice exercise and Tutor-Marked Assignment problems you have previously encountered. All areas of the course will be assessed.

It is better to use the time between finishing the last unit and sitting for the examination to revise the whole course. You might find it useful to review your self-test, TMAs and comments on them before the examination. The end of course examination covers information from all parts of the course.

Course Marking Scheme

Assignment	Marks
Assignments 1- 4	Four assignments, best three marks of the four count at 10% each – 30% of course marks.
End of course examination	70% of overall course marks.
Total	100% of course materials.

Facilitators/Tutors and Tutorials

There are 16 hours of tutorials provided in support of this course. You will be notified of the dates, times and location of these tutorials as well as the name and phone number of your facilitator, as soon as you are allocated a tutorial group.

Your facilitator will mark and comment on your assignments, keep a close watch on your progress and any difficulties you might face and provide assistance to you during the course. You are expected to mail your Tutor-Marked Assignment to your facilitator before the schedule date (at least two working days are required). They will be marked by your tutor and returned to you as soon as possible.

Do not delay to contact your facilitator by telephone or e-mail if you need assistance.

The following might be the circumstances in which you would find assistance necessary, hence you would have to contact your facilitator if:

You do not understand any part of the study or the assigned readings
You have difficulty with the self-tests
You have a question or problem with an assignment or with the grading of an assignment.

You should endeavour to attend the tutorials. This is the only chance to have face to face contact with your course facilitator and to ask questions which are answered instantly. You can raise any problem encountered in the course of your study.

To gain much benefit from course tutorials, prepare a question list before attending them. You will learn a lot from participating actively in discussions.

Summary

Introduction to Petroleum Chemistry is a course that intends to provide the concept of the discipline and is concerned with basic processes and the entire system of petroleum generation, extraction and purification. Upon completing this course, you will be equipped with the basic knowledge of crude oil and natural gas, generation, distribution and purification. In addition, you will be able to answer the following type of questions:

What is crude oil?
What is natural gas?
Of what importance is crude oil and natural gas to national development?
Define the term crude oil.
Define natural gas.
Discuss the different stages of petroleum generation.
Define the term organic matter, and source rock.
Discuss the role of photosynthesis in crude oil generation.
What is diagenesis, catagenesis and metagenesis?

Definitely, this list of questions that you can answer is not limited to the above. To gain the most from this course you should endeavour to apply the principles you have learnt to your understanding of Petroleum Chemistry.

I wish you success in the course and I hope that you will find it both interesting and useful.

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MODULE 1 BASIC CONCEPTS IN PETROLEUM CHEMISTRY

UNIT 1 ORIGIN OF CRUDE OIL

CONTENTS

1.0 INTRODUCTION

This unit will explain petroleum and its origin. It will also introduce you to generation of petroleum (crude oil) and the link between crude oil and photosynthesis. In addition, the importance of carbon cycle in maintaining the carbon balance as well as the fate of organic matter in sediments *viz-a-viz* the three main stages of transformation of organic matter in sediments will also be discussed.

2.0 OBJECTIVES

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

define crude oil
describe the involvement of photosynthesis in production of crude oil
explain the carbon cycle
show diagrammatically the carbon cycle
describe the three main stages of organic matter in sediments: diagenesis, catagenesis and metagenesis.

3.0 MAIN CONTENT

3.1 Definition of Petroleum (Crude oil)

Petroleum can be broadly defined as the complex mixture of hydrocarbons that occurs in the earth in liquid, gaseous, or solid forms. It is a naturally-occurring brown to black flammable liquid (Fig. 1). Crude oils are principally found in oil reservoirs associated with sedimentary rocks beneath the earth's surface.

Fig.1: A Sample of Medium Heavy Crude Oil
(Source: http//www.wikipedia.org*)*

3.2 Generation of Petroleum (Crude oil)

Although exactly how crude oil originated is not established, it is generally agreed that crude oil is derived from marine animal and plant debris subjected to high temperatures and pressures. It is also suspected that the transformation may have been catalysed by rock constituents. Regardless of their origins, crude oil is mainly constituted of hydrocarbons mixed with variable amounts of sulphur, nitrogen, and oxygen compounds. Metals in the forms of inorganic salts or organometallic compounds are present in the crude mixture in trace amounts, the ratio of the different constituents in crude oil, however, varies appreciably from one reservoir to another.

Petroleum generation occurs over long periods of time—millions of years. In order for petroleum generation to occur, organic matter such as dead plants or animals must accumulate in large quantities. The organic matter can be deposited along with sediments and later buried as more sediments accumulate on top. The sediments and organic material that accumulate are called source rock. After burial, chemical activity in the absence of oxygen allows the organic material in the source rock to change into petroleum without the organic matter simply rotting. A good petroleum source rock is a sedimentary rock such as shale or limestone that contains between 1and 5% organic carbon.

Rocks occur in many environments, including lakes, deep areas of the seas and oceans, and swamps. The source rocks must be buried deep enough below the surface of the earth to heat up the organic material, but not so deep that the rocks metamorphose or that the organic material changes to graphite or materials other than hydrocarbons. Temperatures of less than 302°F (150°C) are typical for petroleum generation.

Geologists often refer to the temperature range in which oil forms as an "oil window" below the minimum temperature oil remains trapped in the form of kerogen, and above the maximum temperature the oil is converted to natural gas through the process of thermal cracking. Although this temperature range is found at different depths below the surface throughout the world, a typical depth for the oil window is 4–6 km. Sometimes, oil which is formed at extreme depths may migrate and become trapped at much shallower depths than where it was formed. The Athabasca Oil Sands is an example of this.

According to generally accepted theory, petroleum is derived from ancient biomass. The theory was initially based on the isolation of molecules from petroleum that closely resemble known biomolecules **(**Fig. 2**)**. A number of geologists in Russia adhere to the abiogenic petroleum origin hypothesis and maintain that hydrocarbons of purely inorganic origin exist within Earth's interior. Astronomer Thomas Gold championed the theory in the Western world by supporting the work done by Nikolai Kudryavtsev in the 1950s. It is currently supported primarily by Kenney and Krayushkin.

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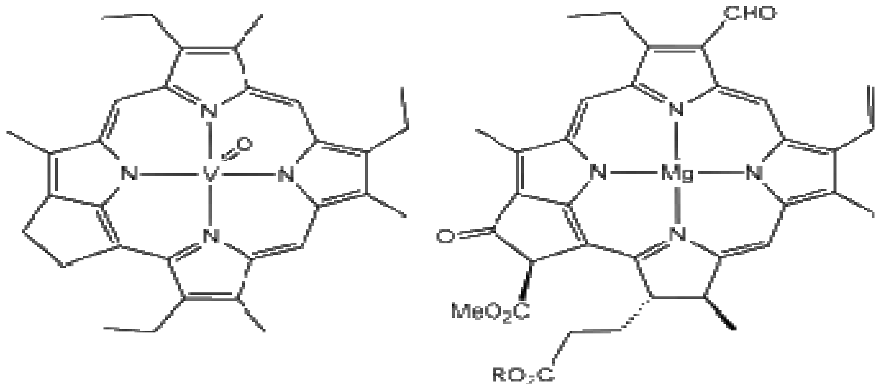

Fig. 2: Structure of Vanadium porphyrin compound (left) extracted from petroleum by Alfred Treibs, father of organic geochemistry. Treibs noted the close structural similarity of this molecule and chlorophyll (right)

Biomass, a renewable energy source, is biological material derived from living, or recently living organisms, such as wood, waste, and alcohol fuels. Biomass is commonly plant matter grown to generate electricity or produce heat. For example, forest residues (such as dead trees, branches and tree stumps), yard clippings and wood chips may be used as biomass. However, biomass also includes plant or animal matter used for production of fibers or chemicals. Biomass may also include biodegradable wastes that can be burnt as fuel. It excludes organic material such as fossil fuels which have been transformed by geological processes into substances such as coal or petroleum. Although fossil fuels have their origin in ancient biomass, they are not considered biomass by the generally accepted definition because they contain carbon that has been "out" of the carbon cycle for a very long time. Their combustion therefore disturbs the carbon dioxide content in the atmosphere.

The abiogenic origin hypothesis lacks scientific support. Extensive research into the chemical structure of kerogen has identified algae as the primary source of oil. The abiogenic origin hypothesis fails to explain the presence of these markers in kerogen and oil, as well as failing to explain how inorganic origin could be achieved at temperatures and pressures sufficient to convert kerogen to graphite. It has not been successfully used in uncovering oil deposits by geologists, as the hypothesis lacks any mechanism for determining where the process may occur.

3.3 Production and Accumulation of Organic Matter

In spite of the common occurrence of petroleum, and the great amount of scientific research on it that has been carried out by many researchers, there remain many unresolved questions regarding its origin. Although it is recognised that the original source of carbon and hydrogen in petroleum was in the original materials that made up the primordial earth, it is generally accepted that these two elements have to pass through an organic phase to be combined into the varying complex molecules recognised as petroleum. There are numerous geochemical and geological reasons for this belief, a few of which are listed below:

Petroleum is commonly associated with sedimentary rocks, principally those deposited under marine conditions but also including continental sediments. Conversely, there is a complete absence of commercial deposits of petroleum where only igneous or metamorphic rocks are present.

The optical activity of petroleum (the ability to rotate the plane of polarised light) is almost completely confined to compounds of biogenic origin.

Most types of petroleum contain complex hydrocarbon compounds termed porphyrins, formed either from the green colouring matter of plants (chlorophyll) or from the red colouring matter of blood (hemin).
Carbon isotope ratios ($^{12}C/^{13}C$) indicate that petroleum may be derived in large part from the lipid (fats and waxes) fractions of organisms.
Many petroleum-like hydrocarbons have been found in recent marine sediments as well as in soils in many places throughout the world. This occurrence forms a link between present living organisms and the petroleum found in sediments of older geological ages.

Thus, in order to produce petroleum, organic matter has to be synthesised by living organisms and thereafter deposited and preserved in sediments. Depending on further geological events, part of the sedimentary organic matter may be transformed into petroleum-like compounds called source rock. It is important to realise that during the history of the earth the conditions for synthesis, deposition and preservation of organic matter have changed.

SELF ASSESSMENT EXERCISE 1

1. What is petroleum?
2. Why it is that crude oil cannot be used directly for the production of chemicals?
3. What are the constituents of crude oil?
4. What are kerogens?

3.4 Organic Source Materials

The organic material that is the source of most petroleum has probably been derived from the single-celled planktonic (free-floating) plants such as diatoms and blue green algae, and single celled planktonic animals such as foraminifers, that live in fresh water. These simple forms were abundant in seas long before the beginning of the Paleozoic Era (The Paleozoic covers the period from the first appearance of abundant, soft-shelled fossils to when the continents were beginning to be dominated by large, relatively sophisticated reptiles and modern plants) 570,000,000 years ago, and could have formed the source organisms of the petroleum found in the Precambrian and early Paleozoic rocks they also may have contributed to much of the petroleum found in younger rocks. In addition, land plants brought into the lakes and seas by rivers apparently have been the source of some crude oils. The larger, more complex forms of sea life-such as corals, mollusks, crustaceans and shellfish are neither abundant enough nor are their remains adequately preserved from the sea scavengers to constitute a source for crude oil.

All organic matter can be divided into the classes of proteins (amino acids), carbohydrates (sugars, cellulose), lignin, pigments (including porphyrins), and lipids (fats, fatty acids). All but lignin are present in both living plants and animals the source materials for petroleum are among these five building blocks of living organisms.

The proteins and their amino acids are relatively easily decomposed and probably contribute little to the petroleum source material (organic matter). Carbohydrates make up the major portion of both plant and animal matter. They are subject to rapid and nearly total degradation but may provide a logical source material for some petroleum.

Lignins must definitely be considered as a major contributor to organic deposits of land plants, and although these have contributed largely to lignite and coal deposits, many authorities believe that they may constitute a progenitor of petroleum hydrocarbons as well. The pigments, particularly the porphyrins, are known to form a minor but recognisable source of crude oil.

It is lipids, however, that may form the chief and primary source of petroleum. Biochemically the lipids (fats and fatty acids) are insoluble in water but are soluble in ether, benzene, or chloroform. Some of the planktonic plants (phytoplanktons) produce and store fatty oils during photosynthesis. Moreover the $^{13}C/^{12}C$ ratios in petroleum closely resemble the ratios found in the lipid fractions of the various phytoplanktons. Because the lipid fraction, which contains the hydrocarbons most closely resembling petroleum, it is much more stable than the water-soluble proteins and carbohydrates. It could well be the main building block from which petroleum is constructed.

3.5 Photosynthesis: the Basis for Mass Production of Organic Matter

Photosynthesis is the basis for the mass production of organic matter. About two billion years ago in Precambrian time, photosynthesis appeared as a worldwide phenomenon.The emergence of photosynthesis as a worldwide phenomenon is a noteworthy historical event with respect to the formation of potential source rocks. Photosynthetic process converts light energy into chemical energy. It is basically a transfer of hydrogen from the water to carbon dioxide to produce organic matter in the form of glucose and oxygen.

The oxygen produced in this reaction is from the water molecule and not from the carbon dioxide. Autotrophic organisms (are organisms that produce their own organic compounds using carbon dioxide from the air or water in which they live) can then synthesise polysaccharide, such as cellulose and starch, and all other necessary constituents from the glucose produced during photosynthesis. Primitive autotrophic organisms, such as photosynthetic bacteria and blue-green algae were the first organisms responsible for this mass production. A basic requirement for photosynthesis is the light absorbing green pigment called chlorophyll (Equation 1)

$$6CO_2 + 12H_2O^* \underset{674Kcal}{\overset{h.v}{\rightleftharpoons}} \underset{\underset{\text{Polysaccaride}}{\downarrow}}{\underset{\textbf{(Glucose)}}{C_6H_{12}O_6}} + 6O_2^* + 6H_2O$$

Equation 1: Equation of Photosynthesis. Glucose relatively rich in energy is formed by green plants with the help of sunlight (h.v). Oxygen is the by-product of this process

You may be wondering that of what significance is photosynthesis to the production of organic matter which eventually leads to the production of source rocks. However, do not lose sight of the fact that without the production of glucose as a result of photosynthesis there will be nothing for autotrophic organisms to synthesise polysaccharide.

3.6 Carbon Cycle

A closer look at the equation of photosynthesis shows that carbon dioxide is used up in the reaction. Since photosynthesis is a continuous process it will come to a time that all the carbon dioxide in the atmosphere will be used up and photosynthesis will come to a stop and subsequently deposition of organic matter will also stop. However, this does not happen, carbon dioxide is reintroduced into the atmosphere. Thus, reintroduction and mass balance of carbon used in photosynthesis is what is known as carbon cycle.

The carbon cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the Earth. The carbon cycle is usually thought of as four major reservoirs of carbon interconnected by pathways of exchange. These reservoirs are:

The plants

The terrestrial biosphere, which is usually defined to include fresh water systems and non-living organic material, such as soil carbon.

The oceans, including dissolved inorganic carbon and living and non-living marine biota.

The sediments including fossil fuels.

The annual movements of carbon, the carbon exchanges between reservoirs, occur because of various chemical, physical, geological, and biological processes. The ocean contains the largest active pool of carbon near the surface of the Earth, but the deep ocean part of this pool does not rapidly exchange with the atmosphere. The global carbon budget is the balance of the exchanges (incomes and losses) of carbon between the carbon reservoirs or between one specific loop (e.g., atmosphere ↔ biosphere) of the carbon cycle. An examination of the carbon budget of a pool or reservoir can provide information about whether the pool or reservoir is functioning as a source or sink for carbon dioxide.

Most of the carbon on earth is concentrated in sedimentary rocks of the earth’s crust. Part of it is fixed as organic carbon, and a greater part as carbonate carbon i.e. compounds containing carbonate anion. A relationship of course exists between organic carbon and carbonate carbon. The atmospheric carbon dioxide reservoir is in a constant exchange with the hydrospheric carbon dioxide reservoir. From aquatic environments, carbonates may be precipitated or deposited by organisms (shells, skeleton etc.) to form carbonate sediments. Conversely, carbonate rocks may be dissolved to contribute to the equilibrium reaction between CO_3^{2-}, HCO_3^- and CO_2 in waters.

Primary organic matter is formed directly from the atmospheric reservoir by terrestrial plants, or by photosynthesis of marine plants from dissolved CO_2 in the hydrosphere.

Terrestrial and marine organic matter, in turn, is largely destroyed by oxidation. Thus, CO_2 is returned for re-circulation in the system. A simplified sketch showing the main processes and pathways concerning the element carbon in the earth’s crust is given in Figure 3. Only an almost negligible portion of the organic carbon in the earth’s crust, including the hydrosphere, is found in living organisms and in dissolved state.

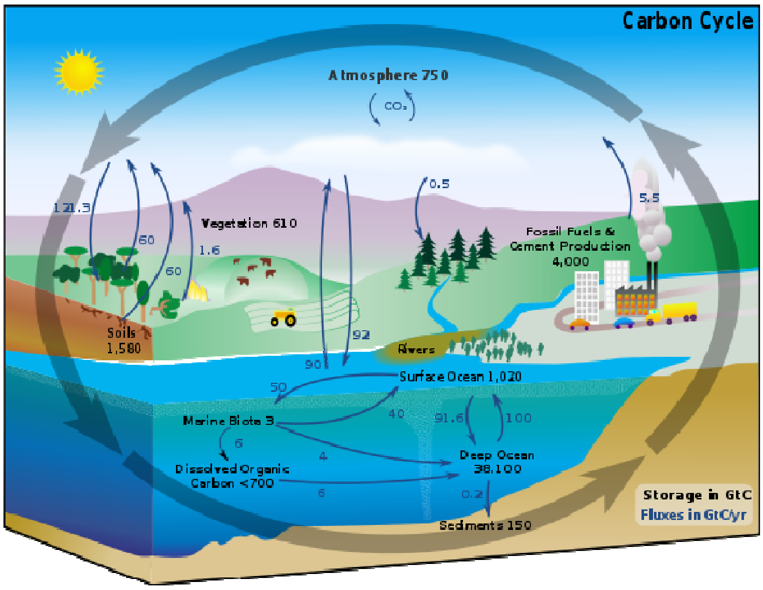

Fig. 3 : Diagram of the Carbon Cycle

The black numbers indicate how much carbon is stored in variousreservoirs, in billions of tons ("GtC" stands for GigaTons of Carbon and figures are circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the 70 million GtC of carbonate rock and kerogen.

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

SELF ASSESSMENT EXERCISE 2

1. Explain the term autotrophic organism.
2. List the four major reservoirs of carbon.
3. What information can you obtain by examining the budget of a pool or reservoir.

4.0 CONCLUSION

This unit has examined the origin of petroleum, what crude oil is and its generation. Also, it has showed the link between photosynthesis and crude oil. Photosynthesis as the basis for mass accumulation of organic matter was also discussed. In addition, the role of carbon cycle in reintroducing and maintaining mass balance of carbon dioxide used in photosynthesis was also examined.

5.0 SUMMARY

This unit has introduced you to the origin of crude oil, the prerequisite for the existence of petroleum source rock. Furthermore, it defined organic matter or material as materials comprised of organic molecules in monomeric or polymeric forms, derived directly or indirectly from organic parts of organisms. In addition, it divides all organic matters into five classes namely proteins (amino acids), carbohydrates (sugar, cellulose), lignin, pigments (including porphyrins) and lipids.

Finally, the unit has also introduced you to conditions necessary for the production of petroleum which include synthesis of organic matter by living organisms, deposition and preservation of such organic matter.

6.0 TUTOR-MARKED ASSIGNMENT

1. What are the facts that support the theory that carbon and hydrogen found in crude oil were in the original materials that made up primordial earth i.e. organic.
2. State why abiogenetic theory / hypothesis failed.
3. Define the following terms:

a. Oil window
b. Source rock
c. Paleozoic era
d. Precambrian era

7.0 REFERENCES/FURTHER READING

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UNIT 2 FATE OF ORGANIC MATTER IN SEDIMENTARY BASINS

CONTENTS

1.0 INTRODUCTION

This unit will discuss the transformation of organic matter deposited in sediments. It will also discuss the various geological boundary conditions controlling the accumulations of organic in sediments.

Furthermore, it will discuss the physicochemical transformation of organic matter in sediments, and will also discuss factors that determine the variation of sediments. A general scheme of evolution of organic matter from time of deposition in sediments will also be examine. In order to understand the discussion the following stages of evolution: diagenesis, catagenesis, metagenesis and metamorphism will be considered.

2.0 OBJECTIVES

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

state the favourable conditions for the deposition of sediments rich in organic matter
define and discuss diagenesis, catagenesis and metagenesis
explain transformation of organic matter.

3.0 MAIN CONTENT

3.1 Accumulation of Organic Matter

Production, accumulation and preservation of undegraded organic matter are prerequisites for the existence of petroleum. It should be noted that the term “organic matter’ does not include mineral skeletal parts, such as shells, bones, and teeth. The accumulation of organic matter in sediments is controlled by a number of geological boundary conditions. It is practically restricted to sediment deposited in aquatic environments, which must receive a certain minimum amount of organic matter. This organic matter can be supplied either in the form of dead or living particulate organic matter or as a dissolved organic matter. The organic material may be autochthonous to the environment where it is deposited, that is, it originated in the water column above or within the sediment in which it is buried, or it may be allochthonous, i.e., foreign to its environment of deposition. Both the energy situation in the water body in question and the supply of mineral sedimentary particles must be such as to allow a particular kind of sedimentation. If the energy level in a body of water is too high, either there is erosion of sediment rather than deposition, or deposited sediment is too coarse to retain low-density organic material. An example is a beach area with strong wave action. Furthermore, in coarse-grained sediment, ample diffusion of oxygen is possible through the wide open pores. On the other hand, if the level of energy is very low, too little sediment is supplied, and there is, like-wise, no appreciable organic sedimentation. Examples of this type occur in certain parts of the deep sea.

Once these boundary conditions are satisfied, the accumulation of organic matter in sediment is dependent on the dualism between processes that conserve and concentrate and those that destroy and dilute organic matter.

3.2 Diagenesis

Sediments deposited in sub-aquatic environments contain large amounts of water (the amount of water is 60% of the total weight of sediment), minerals, dead organic material, and numerous living microorganisms. Such a mixture results from various sedimentary processes and primary components of very different origin it is not in equilibrium and therefore unstable, even if microorganisms are not present. Diagenesis is a process through which the system tends to approach equilibrium under conditions of shallow burial, and through which the sediment normally becomes consolidated. The depth interval concerned is in the order of a few hundred meters, occasionally to a few thousand meters. In the early

diagenetic process, the increase in temperature and pressure is small and transformation of the sediments occurs under mild conditions.
During early diagenesis, microbial activity transforms the sediment. Anaerobic organisms reduce sulphates to free oxygen; the oxygen so produced is consumed by aerobic microorganisms that live in the uppermost layer of sediments. The energy required is provided by the decomposition of organic matter, which in the process is converted into carbon dioxide, ammonia and water. The conversion is usually carried out completely in sands and partly in mud. During this period, the Eh decreases abruptly and the pH increases slightly. In addition, certain solids like $CaCO_3$ and SiO_2 dissolve and reach saturation and re-precipitate, together with authigenic minerals such as sulphides of iron, copper, lead and zinc.

Within the sediment, organic material proceeds towards equilibrium. Furthermore, during diagenesis proteins and carbohydrates (known as biogenic polymers or biopolymers) are destroyed by microbial activity. Their constituents become progressively engaged in new polycondensed structures leading to the production of *kerogen*. Kerogen is the organic constituent of sedimentary rocks that is not soluble in aqueous alkaline solvents or in common organic solvents. The part of the sedimentary rock that is soluble in organic solvents is known as bitumen. Kerogen is the most important form of organic carbon on earth, and it is 100 times more abundant than coal plus petroleum in reservoirs, and is 50 times more abundant than bitumen. Kerogens that have a high hydrogen / carbon ratio have potential for oil and gas generation. Thus diagenesis begins in recently deposited sediments where microbial activity occurs. At the end of diagenesis, the organic matter consists mainly of a fossilised, insoluble organic residue called kerogen.

3.3 Catagenesis

Continuous deposition of sediments results in the burial of previous bed to a depth reaching several kilometers of overburden in subsiding basins. This leads to a considerable increase in temperature and pressure. Such increase again places the system out of equilibrium and results in new changes. There are some changes in the clay fraction while the mineral phase’s composition and texture are conserved. The main inorganic modification at this stage involves the compaction of the rock, water continue to be expelled, porosity and permeability decreases greatly, salinity of the interstitial water increases and may come close to saturation.

On the other hand, liquid petroleum is first produced by the kerogen generated in the diagenesis stage. In a later stage, wet gas and condensate are produced. Both liquid oil and condensate are accompanied by significant amount of methane. These are the major changes that the organic matter experience during catagenesis.

The end of catagenesis is reached when the disappearance of aliphatic carbon chain in kerogen is completed. Catagenesis results from an increase in temperature during burial in sedimentary basins. Thermal breakdown of kerogen is responsible for the generation of most hydrocarbons.

3.4 Metagenesis

The last stage of the evolution of sediments is known as metagenesis. Metagenesis is reached only at great depth, where temperature and pressure are high. At this stage, organic matter is composed only of methane and a carbon residue. The constituents of residual kerogen are converted to graphite carbon. Minerals are severely transformed under this condition, clay mineral lose their interlayer water and gain a higher stage of crystallinity iron oxides containing structural water (goethite) change to oxides without water (hematite) etc. severe pressure dissolution and recrystallisation occur, like the formation of quartizite, and may result in a disappearance of the original rock structure. The rock reaches temperature conditions that lead to the metagenesis of organic matter. At this stage, the organic matter is composed only of methane and a carbon residue, where some crystalline ordering begins to develop. Coals are transformed into anthracite.

SELF ASSESSMENT EXERCISE

Explain the following terms:

a. Autochthonous
b. Allochthontous

3.5 Transformation of Organic Matter

The time covering sedimentation processes and residence in the young sediment, freshly deposited, represents a very special stage in the carbon cycle. The first few meters of sediment, just below the water-sediment contact, represent the interface through which organic carbon passes from the biosphere to the geosphere. The residence period of organic compounds in this zone of the sedimentary column is long compared to the lifetime of the organisms, but very short compared to the duration of geological cycles e.g. 1-m section often represents 500 to 10000 years.

During sedimentation processes, and later in such young sediments, organic material is subjected to alterations by varying degrees of microbial and chemical actions. As a result, its composition is largely changed and its future fate during the rest of the geological history predetermined within the framework of its subsequent temperature history. When comparing the nature of the organic material in young sediments with that of the living organisms from which it was derived, the striking point is that most of the usual constituents of these organisms, and particularly the biogenic macromolecules, have disappeared. Proteins, carbohydrates, lipids, and lignin in higher plants amount to nearly the total dry weight, on an ash-free basis, of the biomass living in sub-aquatic or sub-aerial environments. The total amount of the same compounds that can be extracted from very young sediments is usually not more than 20% of the total organic material, and often less. This situation results from degradation of the macromolecules by bacteria into individual amino acids, sugars, etc. As monomers, they are used for nutrition of the microorganisms, and the residue becomes polycondensed, forming large amounts of brown material, partly soluble in dilute sodium hydroxide, and resembling humic acids.

As a result of microbial activity in water and in sub-aquatic soils, biogenic polymers have been degraded, then used as much as possible for the metabolism of microorganisms. Thus, even in fine mud, a part of the organic matter has been consumed and has disappeared through conversion into carbon dioxide and water. Another part has been used to synthesise the constituents of the microbial cell, and thus is reintroduced into the biological cycle. The residue that cannot be incorporated by microorganisms is now incorporated into a new polycondensate, which is insoluble kerogen. This chemical process occurs under mild temperature and pressure conditions. Thus, the influence of the increase of temperature and pressure is likely to be subordinate, compared to the nature of the original organic constituents. This view is confirmed by the results of experimental evolution tests of heating organic matter under inert atmosphere in order to stimulate the transformations at greater depth that is catagenesis and metagenesis but not diagenesis.

At the end of diagenesis, organic matter still comprises minor amount of free hydrocarbons and related compounds. They have been synthesised by living organisms and incorporated in the sediment with no or minor changes. Thus, they can be considered as geochemical fossils, witnessing the depositional environment. As time and sedimentation proceed, the sediment is buried to several hundreds of meters. Most of the organic material becomes progressively insoluble as a result of increasing polycondensation associated with loss of superficial hydrophilic functional groups. This completely insoluble organic matter from sediments has received limited attention until recently. It is called "*humin*" by the few soil scientists who have worked on sub-aquatic soils. In ancient sediments, the insoluble organic matter is called *kerogen* and is obtained by demineralisation of the rock. The terms *humin* and *kerogen* are not strictly equivalent thus, humin, collectively with other insoluble organic matter such as pollen, spores, etc. may be considered as a precursor of kerogen. Petroleum geochemists consider kerogen as the main source of petroleum compounds. The whole process is referred to as diagenesis and leads from biopolymers synthesised by living organisms to geopolymers (kerogen) through fractionation i.e. by separating the mixture into its components, partial destruction and rearrangement of the building blocks of the macromolecules. The transformation of sediments to kerogen can be assumed to occur or takes place in three steps viz-a-viz biochemical degradation, polycondensation and insolubilisation.

Kerogen is a mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks. It is insoluble in normal organic solvents because of the huge molecular weight (upwards of 1,000 Daltons) of its component compounds. The soluble portion is known as bitumen. When heated to the right temperatures in the Earth's crust, (*oil window* ca. 60°-120°C, *gas window* ca. 120°-150°C) some types of kerogen release crude oil or natural gas, collectively known as hydrocarbons (fossil fuels). When such kerogens are present in high concentration in rocks such as shale they form possible source rocks. Shales rich in kerogens that have not been heated to a sufficient temperature to release their hydrocarbons may form oil shale deposits. As kerogen is a mixture of organic material, rather than a specific chemical, it cannot be given a chemical formula. Indeed its chemical composition can vary distinctively from sample to sample. Kerogen from the Green River Formation oil shale deposit of western North America contains elements in the proportions C 215 : H 330 : O 12 : N 5 : S 1.

There are three types of kerogen namely labile kerogen, refractory kerogen and inert kerogen. Labile kerogen breaks down to form heavy hydrocarbons (i.e. oils), refractory kerogen breaks down to form light hydrocarbons (i.e. gases), and inert kerogen forms graphite. However, when Van Krevelen diagram is used (Van Krevelen diagrams are a graphical-statistical method that cross-plots the oxygen: carbon and hydrogen: carbon ratios of petroleum) to classify kerogen. The following types of kerogen are arrived at:

Type I

> Containing alginite, amorphous organic matter, cyanobacteria, freshwater algae, and land plant resins
> Hydrogen:Carbon ratio > 1.25

Oxygen:Carbon ratio < 0.15
Shows great tendency to readily produce liquid hydrocarbons.
It derives principally from lacustrine algae and forms only in anoxic lakes and several other unusual marine environments
Has few cyclic or aromatic structures
Formed mainly from proteins and lipids

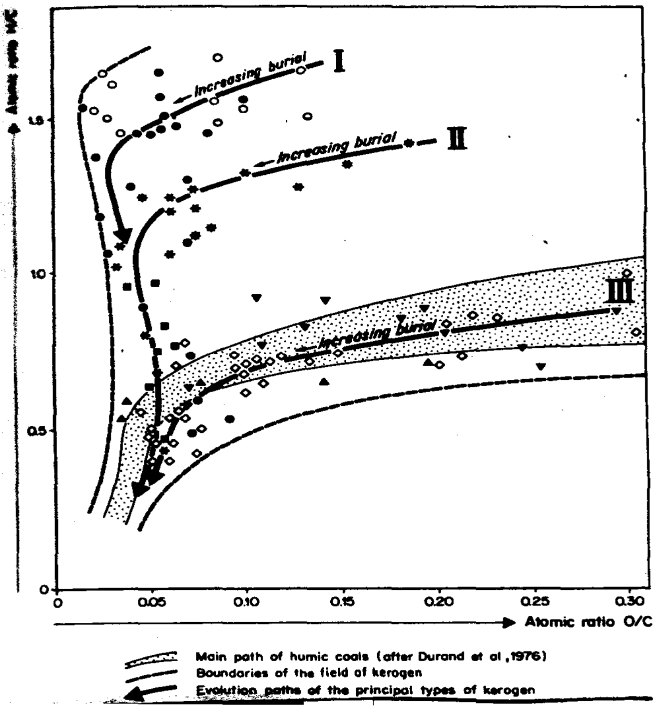

Fig. 1 : Van Krevelen Diagram (Principal types and evolution path of kerogen: types I, II and III are most frequent. Kerogen of intermediate composition also occurs. Evolution of kerogen composition with increasing burial is marked by an arrow along each evolution path I, II, and III

(*Source*: Petroleum formation and occurrence. B. R. Tissot & D. W. Welte)

Type II

Hydrogen:Carbon ratio < 1.25
Oxygen:Carbon ratio 0.03 to 0.18
Tend to produce a mix of gas and oil.
Several types: exinite, cutinite, resinite, and liptinite
Exinite: formed from the casings of pollen and spores
Cutinite: formed from terrestrial plant cuticle
Resinite: formed from terrestrial plant resins and animal decomposition resins

Liptinite: formed from terrestrial plant lipids (hydrophobic molecules that are soluble in organic solvents) and marine algae
They all have great tendencies to produce petroleum and are all formed from lipids deposited under reducing conditions.

Type II-Sulphur

Similar to Type II but high in sulphur.

Type III

Hydrogen:Carbon ratio < 1
Oxygen:Carbon ratio 0.03 to 0.3
Material is thick, resembling wood or coal.
Tends to produce coal and gas (recent research has shown that type III kerogens can actually produce oil under extreme conditions).
Has very low hydrogen because of the extensive ring and aromatic systems

Kerogen Type III is formed from terrestrial plant matter that is lacking in lipids or waxy matter. It forms from cellulose, the carbohydrate polymer that forms the rigid structure of terrestrial plants, lignin, a non-carbohydrate polymer formed from phenyl-propane units that binds the strings of cellulose together, and terpenes and phenolic compounds in the plant.

Most of the biomass that eventually becomes petroleum is contributed by the bacteria and protists that decompose the primary matter, not the primary matter itself. However, the lignin in this kerogen decomposes to form phenolic compounds that are toxic to bacteria and protists. Without this extra input, it will only become methane and/or coal.

Type IV (Residue)

Hydrogen:Carbon < 0.5

Type IV kerogen contains mostly decomposed organic matter in the form of polycyclic aromatic hydrocarbons. They have no potential to produce hydrocarbons.

3.6 From Kerogen to Petroleum

As sedimentation and subsidence continue, temperature and pressure increase. In this changing physical environment, the structure of the immature kerogen is no longer in equilibrium with its surroundings.

Rearrangements will progressively take place to reach a higher, and thus more stable, degree of ordering. The steric hinderances for higher ordering have to be eliminated. They are, for instance, nonpolar cycles (e.g., saturated cycles) and linkages with or without heteroatoms, preventing the cyclic nuclei from a parallel arrangement.

This constant adjustment of kerogen to increasing temperature and pressure results in a progressive elimination of functional groups and of the linkages between nuclei (including carbon chains). A wide range of compounds is formed, including medium to low molecular weight hydrocarbons, carbon dioxide, water, hydrogen sulphide, etc. Therefore, the petroleum generation seems to be a necessary consequence of the drive of kerogen to adjust to its new surroundings by gaining a higher degree of order with increasing overburden.

Kerogen is a polycondensed structure formed under the mild temperature and pressure conditions of young sediments and metastable under these conditions. Therefore, its characteristics seem to remain rather constant, even in ancient sediments, as long as they are not buried deeply. In most cases, however, as sedimentation and subsidence proceed, kerogen is subjected to a progressive increase of temperature and pressure. It is no longer stable under the new condition. Rearrangements occur during the successive stages of diagenesis, catagenesis, and metagenesis toward thermodynamic equilibrium.

Diagenesis of kerogen is marked by decrease of oxygen and a corresponding increase of carbon content with increasing depth. With reference to van Krevelen diagram (Figure 1), this stage of evolution results in a slight decrease in the ratio of hydrogen / carbon and a marked decrease of oxygen / carbon. Infrared spectroscopy has demonstrated that the decrease of oxygen is due essentially to the progressive elimination of carbonyl (C=O) group. In terms of petroleum exploration, this stage corresponds to an immature kerogen, and little hydrocarbon generation has occurred in the source rock. However, large quantities of carbon dioxide and water and also some heavy heteroatomic (N, S, O) compounds may be produced in relation to oxygen elimination.

Catagenesis, the second stage of kerogen degradation, is marked by an important decrease of the hydrogen content and of the hydrogen to carbon ratio, due to generation and release of hydrocarbons. Again, in terms of petroleum exploration, the stage of catagenesis corresponds to the main zone of oil generation and also to the beginning of the cracking zone, which produces “wet gas” with a rapidly increasing proportion of methane. As temperature continues to increase, the kerogen reaches the stage of catagenesis. More bonds of various types are broken, like esters and also some carbon –carbon bonds, within the kerogen and within the previously generated fragments. The new fragments generated become smaller and devoid of oxygen, therefore, hydrocarbons are relatively enriched. This corresponds first to the principal phase of oil formation, and then to the stage of “wet gas” and condensate generation. At the same time, the carbon content increases in the remaining kerogen, due to the elimination of hydrogen. Aliphatic and alicyclic groups are partly removed from kerogen, carbonyl and carboxyl groups are completely eliminated, and most of the remaining oxygen is included in either bonds and possibly in heterocyclic.

When the sediment reaches the deepest part of the sedimentary basins, temperatures become quite high. A general cracking of carbon – carbon bond occurs, both in kerogen and bitumen already generated from it. Aliphatic groups that were still present in kerogen almost disappear, correspondingly, low molecular weight compound, especially methane, are released. The remaining sulphur, when present in kerogen, is mostly lost, and H_2S generation may be important. This is the principal phase of dry gas formation.

Once most labile functional groups and chains are eliminated, aromatisation and polycondensation of the residual kerogen increases, as shown by alteration of optical characteristics and by Infra-Red spectra. Parallel arrangement of aromatic nuclei extends over wide areas from 80 to 500Å, forming clusters. Physical properties evolve accordingly (high reflectance, electron diffraction). Such residual kerogen is unable to continue to generate hydrocarbons, as shown by the negative results of thermo-gravimetric assays. This stage is reached only in deep or very old sedimentary basins and it corresponds to metagenesis.

SELF ASSESSMENT EXERCISE 2

1. What is the effect of too high energy in a body of water on sedimentation?
2. What is the effect of very low energy in a body of water on sedimentation?

4.0 CONCLUSION

This unit discussed the production, accumulation and preservation of undegraded organic matter in sediments. It also discussed the various geological boundary conditions controlling the accumulation of organic matter in sediments.

In addition, this unit also discussed all the four stages of organic matter evolution in sediments. It further examined the meaning of kerogen and the van Krevelen diagram as a graphical-statistical method used in classifying kerogen. Finally, the different types and the transformation of kerogen to petroleum were discussed.

5.0 SUMMARY

This unit has introduced you to the production, accumulation and preservation of organic matter, the various physico-chemical transformations of organic matter to kerogen, the different types of kerogen and the Van krevelen diagram was also introduced.

Furthermore, the unit classified kerogens into three types. The kerogens were classified by their respective evolution path in the Van krevelen diagram.

6.0 TUTOR-MARKED ASSIGNMENT

1. List and briefly discuss the three main stages of evolution of organic matter.
2. Kerogen can be classified into three types. Discuss.
3. What are the geological boundary conditions that control the accumulation of organic matter in sediments?
4. Physicochemical transformation of organic matter is controlled by certain factors, list them.
5. What are the prerequisites for the existence of petroleum?

7.0 REFERENCES/FURTHER READING

Matar, S. & Hatch, L.F. (1994). *Chemistry of Petrochemical Processes*. (2nd ed.). Houston: Gulf Publishing Company.

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UNIT 3 GAS ORIGIN, TRANSPORTATION AND USES

CONTENTS

1.0 INTRODUCTION

Natural gas is a gas consisting primarily of methane. It is found associated with fossil fuels, in coal beds, as methane clathrates, and is created by methanogenic organisms in marshes, bogs, and landfills. It is an important fuel source, a major feedstock for fertilizers, and a potent greenhouse gas. It is often informally referred to as simply gas, especially when compared to other energy sources such as electricity. This unit will examine the origin, generation and migration of natural gas. It will also examine the differences between natural and other gases. Furthermore, processing, uses, environmental effect, energy content, statistics and pricing of natural gas will also be discussed.

2.0 OBJECTIVES

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

discuss the origin of natural gas
explain the accumulation of natural gas
differentiate between natural gas and other gases
describe the process of natural gas using processing plant
list uses of natural gas.

3.0 MAIN CONTENT

3.1 Origin of Natural Gas Accumulations

The decomposition of organic material in an oxygen-poor environment, with the aid of anaerobic bacteria, results in the formation of methane. Since organic matter is present in the younger sediments of the earth, so is methane. If all of the existing methane could be collected, it could provide most of the world's energy for hundreds of years. Unfortunately, most is too diffuse to be commercially recovered. Natural gas, a hydrocarbon mixture consisting primarily of methane and ethane, is derived from both land plant and marine organic matter. Over geologic time, almost all natural gas reaches the earth's surface and is lost to the atmosphere. When its upward migration is interrupted by a geologic trap (an upwardly convex permeable reservoir rock sealed above by impermeable cap rock) commercial quantities of gas can accumulate. This gas is termed non associated gas. Commercial amounts of gas also can accumulate as a gas cap above an oil pool or, if reservoir pressure is sufficiently high, dissolved in the oil. Such natural gas is termed associated gas.

Natural gas generation and migration occurs over an extensive vertical zone that includes shallow biogenic gas, intermediate dissolved gas of the oil window, and deep thermal gas. The production of biogenic methane requires anaerobic microbial activity, and is confined to poorly drained swamps, some lake bottoms, and marine environments below the zone of active sulphate reduction. Gas of predominantly biogenic origin constitutes more than 20 percent of global gas reserves. The mature stage of petroleum generation occurs at depths between about 6,500 and 16,000 feet, depending upon the geothermal gradient. At these temperatures and pressures, the full range of hydrocarbons is produced within the oil window and significant amounts of thermal methane gas often are generated along with the oil. Below about 9,500 feet, primarily wet gas that contains liquid hydrocarbons is formed. In the post mature stage, beneath about 16,000 feet, oil is no longer stable and the main hydrocarbon product is thermal methane gas that is a product of the cracking of the existing liquid hydrocarbons.

Gas displays an initial low concentration and high dispersibility, making adequate seals very important to conventional gas accumulation. Due to differences in the physical properties of gas and oil, similarly sized oil traps contain more recoverable energy (on a Btu basis) than gas traps, although more than three-quarters of the in-place gas often can be recovered. Less than one percent of the gas fields of the world are of giant size, originally containing at least 3 trillion cubic feet of recoverable gas. These fields, however, along with the associated gas in giant oil fields, account for about 80% of the world’s proved and produced gas reserves. Oil is derived mainly from marine or lacustrian source rocks, but, since gas can be derived from land plants as well, all source rocks have the potential for gas generation. Many large gas accumulations appear to be associated with the coal deposits.

3.2 Unconventional Gas Accumulations

The boundary between conventional gas and unconventional gas resources is not well defined, because they result from a continuum of geologic conditions. Coal seam, shale, and tight gas occur in rocks of low permeability and require special treatment for recovery. The process by which vegetation is converted to coal over geologic time generates large amounts of natural gas. Much of this gas becomes concentrated as conventional gas deposits in permeable sediments adjacent to the coal, but some gas remains in the coal as unconventional “continuous" gas deposits. The coal does not form a continuous reservoir over an entire basin, but occurs in individual non-communicating coal seams separated by other strata. Coal seams are compartmentalised gas reservoirs bounded by facies changes or faults and the coal itself yields extremely variable amounts of gas. Coal seams that are deeply buried exhibit significantly reduced permeabilities and, thus, reduced gas recoverability.

Coal seam gas well productivity depends mostly on reservoir pressure and water saturation. Multi-well patterns are necessary to remove water from the coal and to establish a favorable pressure gradient. Since the gas is adsorbed on the surface of the coal and trapped by reservoir pressure, initially there is low gas production and high water production. Therefore, an additional expense relates to the disposal of coal bed water, which may be saline, acidic, or alkaline. As production continues, water production declines and gas production increases, before eventually beginning a long decline. In general, however, coal seam gas recovery rates have been low and unpredictable. Average per-well conventional gas production in a mature gas-rich basin is about five times higher than average per-well coal seam gas production. Thus, several times as many wells have to be drilled in coal seams than in conventional gas accumulations to achieve similar gas recovery levels.

Large continuous gas accumulations are sometimes present in low permeability (tight) sandstones, siltstones, shale, sandy carbonates, limestone, dolomites, and chalk. Such gas deposits are commonly classified as unconventional because their reservoir characteristics differ from conventional reservoirs and they require stimulation to be produced economically. The tight gas is contained in lenticular or blanket reservoirs that are relatively impermeable and can occur downdip from water-saturated rocks and cut across lithologic boundaries. They often contain a large amount of in-place gas, but exhibit low recovery rates. Gas can be economically recovered from the better quality continuous tight reservoirs by creating downhole fractures with explosives or hydraulic pumping. The nearly vertical fractures provide a pressure sink and channel for the gas, creating a larger collecting area so that the gas recovery is at a faster rate. Sometimes massive hydraulic fracturing is required, using a half million gallons of gelled fluid and a million pounds of sand to keep the fractures open after the fluid has been drained away.

In the United States, unconventional gas accumulations account for about 2 trillion cubic feet (tcf) of gas production per year, some 10 per cent of total gas output. In the rest of the world, however, gas is predominantly recovered from conventional accumulations.

3.3 Town Gas

Town gas is a mixture of methane and other gases, mainly the highly toxic carbon monoxide that can be used in a similar way to natural gas and can be produced by treating coal chemically. This is a historic technology, still used as 'best solution' in some local circumstances, although coal gasification is not usually economic at current gas prices. However, depending upon infrastructure considerations, it remains a future possibility.

Most town “gas houses” located in the eastern United States in the late nineteenth and early twentieth centuries were simple by-product of coke ovens which heated bituminous coal in air-tight chambers. The gas driven off from the coal was collected and distributed through town-wide networks of pipes to residences and other buildings where it was used for cooking and lighting purposes. (Gas heating did not come into widespread use until the last half of the twentieth century.) The coal tar that collected in the bottoms of the gas house ovens was often used for roofing and other water-proofing purposes, and also, when mixed with sand and gravel, was used for creating Bitumen for the surfacing of local streets.

3.4 Bio Gas

When methane-rich gases are produced by the anaerobic decay of non-fossil organic matter (biomass), these are referred to as biogas (or natural biogas). Sources of biogas include swamps, marshes, and landfills (see landfill gas), as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle.

Methanogenic archaea are responsible for all biological sources of methane, some in symbiotic relationships with other life forms, including termites, ruminants, and cultivated crops. Methane released directly into the atmosphere would be considered as a pollutant, however, methane in the atmosphere is oxidised, producing carbon dioxide and water. Methane in the atmosphere has a half life of seven years, meaning that every seven years, half of the methane present is converted to carbon dioxide and water.

Future sources of methane, the principal component of natural gas include landfill gas, biogas and methane hydrate. Biogases, and especially landfill gas, are already in used in some areas, but their use could be greatly expanded. Landfill gas is a type of biogas, but biogas usually refers to gas produced from organic material that has not been mixed with other waste.

Landfill gas is created from the decomposition of waste in landfills. If the gas is not removed, the pressure may get so high that it works its way to the surface, causing damage to the landfill structure, unpleasant odour, vegetation die-off and an explosion hazard. The gas can be vented to the atmosphere, flared or burned to produce electricity or heat.

Once water vapour is removed, about half of landfill gas is methane. Almost all of the rest is carbon dioxide, but there are also small amounts of nitrogen, oxygen and hydrogen. There are usually trace amounts of hydrogen sulphide and siloxanes, but their concentration varies widely. Landfill gas cannot be distributed through natural gas pipelines unless it is cleaned up to the same quality. It is usually more economical to combust the gas on site or within a short distance of the landfill using a dedicated pipeline. Water vapour is often removed, even if the gas is combusted on site. Other non-methane components may also be removed in order to meet emission standards, to prevent fouling of the equipment or for environmental considerations. Co-firing landfill gas with natural gas improves combustion, which lowers emissions.
Biogas is usually produced using agricultural waste materials, such as unusable parts of plants and manure. Biogas can also be produced by separating organic materials from waste that otherwise goes to landfills.

This is more efficient than just capturing the landfill gas it produces. The use of materials that would otherwise generate no income or even cost money to get rid of, improves the profitability and energy balance of biogas production.

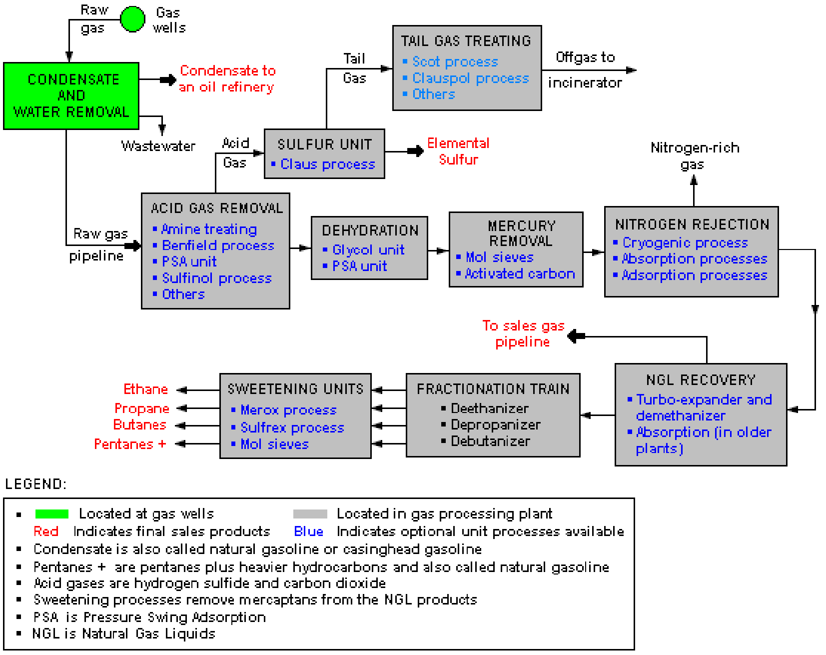
Anaerobic lagoons produce biogas from manure, while biogas reactors can be used for manure or plant parts. Like landfill gas, biogas is mostly methane and carbon dioxide, with small amounts of nitrogen, oxygen and hydrogen. However, with the exception of pesticides, there are usually lower levels of contaminants.

3.5 Hydrates

Huge quantities of natural gas (primarily methane) exist in the form of hydrates under sediment on offshore continental shelves and on land in arctic regions that experience permafrost such as those in Siberia (hydrates require a combination of high pressure and low temperature to form). However, as at 2009, no technology has been developed to produce natural gas economically from hydrates.

3.6 Natural Gas Production

The image below (Fig. 1) is a schematic block flow diagram of a typical natural gas processing plant. It shows the various unit processes used to convert raw natural gas into sales gas pipelined to the end user markets.



- 🟩 Located at gas wells ▨ Located in gas processing plant
- Red Indicates final sales products Blue Indicates optional unit processes available
- Condensate is also called natural gasoline or casinghead gasoline
- Pentanes + are pentanes plus heavier hydrocarbons and also called natural gasoline
- Acid gases are hydrogen sulfide and carbon dioxide
- Sweetening processes remove mercaptans from the NGL products
- PSA is Pressure Swing Adsorption
- NGL is Natural Gas Liquids

Fig. 1: Schematic Flow Diagram of a Typical Natural Gas Processing Plant

(*Source*: http//en.wikipedia.org/wiki/file)

The block flow diagram also shows how processing of the raw natural gas yields by product sulphur, by product ethane, and natural gas liquids (NGL) propane, butane and natural gasoline (denoted as pentanes +).

3.7 Uses of Natural Gas

3.7.1 Power Generation

Natural gas is a major source of electricity generation through the use of gas turbines and steam turbines. Most grid peaking power plants and some off-grid engine-generators use natural gas. This is because high efficiencies can be achieved through combining gas turbines with a steam turbine in combined cycle mode. Natural gas burns more cleanly than other fossil fuels, such as oil and coal, and produces less carbon dioxide per unit energy released.

For an equivalent amount of heat, burning natural gas produces about 30% less carbon dioxide than burning petroleum and about 45% less than burning coal. Combined cycle power generation using natural gas is thus the cleanest source of power available using fossil fuels, and this technology is widely used wherever gas can be obtained at a reasonable cost. Fuel cell technology may eventually provide cleaner options for converting natural gas into electricity, but it is not price-competitive.

3.7.2 Domestic Use

Natural gas is supplied to homes, where it is used for such purposes as cooking in natural gas-powered engines and/or ovens, natural gas-heated clothes dryers, heating/cooling and central heating. Home or other building heating may include boilers, furnaces, and water heaters. Methane also known as compressed natural gas (CNG) is used in rural homes without connections to piped-in public utility services, or with portable grills. However, due to CNG being less economical than liquified natural gas, LPG (Propane) is the dominant source of rural gas.

3.7.3 Transportation Fuel

Compressed natural gas (CNG) is a cleaner alternative to other automobile fuels such as gasoline (petrol) and diesel. The energy efficiency is generally equal to that of gasoline engines, but lower compared with modern diesel engines. Gasoline/petrol vehicles converted to run on natural gas suffer because of the low compression ratio of their engines, resulting in a cropping of delivered power while running on natural gas (10-15%). CNG-specific engines, however, use a higher compression ratio due to its fuel's higher octane number of 120–130.

3.7.4 Fertilizer

Natural gas is a major feedstock for the production of ammonia, via the Haber process, for use in fertilizer production.

3.7.5 Aviation

Russian aircraft manufacturer, Tupolev claims that at current market prices, an LNG-powered aircraft would cost 5,000 rubles (~ $218/ £112) less to operate per ton, roughly equivalent to 60%, with considerable reductions to carbon monoxide, hydrocarbon and nitrogen oxide emissions.

The advantages of liquid methane as a jet engine fuel are that it has more specific energy than the standard kerosene mixes and that its low temperature can help cool the air which the engine compresses for greater volumetric efficiency, in effect replacing an intercooler. Alternatively, it can be used to lower the temperature of the exhaust.

3.7.6 Hydrogen

Natural gas can be used to produce hydrogen, with one common method being the hydrogen reformer. Hydrogen has various applications: it is a primary feedstock for the chemical industry, a hydrogenating agent, an important commodity for oil refineries, and a fuel source in hydrogen vehicles.

3.7.7 Others

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

SELF ASSESSMENT EXERCISE 1

1. What are the by-products of processing raw natural gas?
2. What is the full meaning of NGL?
3. What is the full meaning of CNG?
4. What is the full meaning of LPG?

3.8 Storage and Transport

The major difficulty in the use of natural gas is transportation and storage because of its low density. Natural gas pipelines are economical, but are impractical across oceans.

LNG carriers can be used to transport liquefied natural gas (LNG) across oceans, while tank trucks can carry liquefied or compressed natural gas (CNG) over shorter distances. Sea transport using CNG carrier ships that are now under development may be competitive with LNG transport in specific conditions.

For LNG transport, a liquefaction plant is needed at the exporting end and regasification equipment at the receiving terminal. Shipborne regasification equipment is also practicable. LNG transportation is established as the preferred technology for long distance, high volume transportation of natural gas, whereas pipeline transport is preferred for transport for distances up to 4.000 km overland and approximately half that distance overseas. However, for CNG transport, high pressure, typically above 200 bars, is used. Compressors and decompression equipment are less capital intensive and may be economical in smaller unit sizes than liquefaction/regasification plants. For CNG mode, the crucial problem is the investment and operating cost of carriers. Natural gas trucks and carriers may transport natural gas directly to end-users, or to distribution points such as pipelines for further transport.

In the past, the natural gas which was recovered in the course of recovering petroleum could not be profitably sold, and was simply burned at the oil field (known as flaring). This wasteful practice is now illegal in many countries. Additionally, companies now recognise that value for the gas may be achieved with LNG, CNG, or other transportation methods to end-users in the future. The gas is now re-injected back into the formation for later recovery. This also assists oil pumping by keeping underground pressures higher. The natural gas is used to generate electricity and heat for desalination. Similarly, some landfills that also discharge methane gases have been set up to capture the methane and generate electricity.

Natural gas is often stored underground inside depleted gas reservoirs from previous gas wells, salt domes, or in tanks as liquefied natural gas. The gas is injected during periods of low demand and extracted during periods of higher demand. Storage near the ultimate end-users helps to best meet volatile demands, but this may not always be practicable.

With 15 nations accounting for 84% of the worldwide production, access to natural gas has become a significant factor in international economics and politics. In this respect, control over the pipelines is a major strategic factor.

3.9 Environmental Effect

3.9.1 Climate Change

Natural gas is often described as the cleanest fossil fuel, producing less carbon dioxide per joule delivered than either coal or oil, and far fewer pollutants than other fossil fuels. However, in absolute terms it does contribute substantially to global carbon emissions, and this contribution is projected to grow. According to the IPCC Fourth Assessment Report (Working Group III Report, Chapter 4), in 2004 natural gas produced about 5,300 Mt/yr of CO_2 emissions, while coal and oil produced 10,600 and 10,200 respectively but by 2030, according to an updated version of the SRES B2 emissions scenario, natural gas would be the source of 11,000 Mt/yr, with coal and oil now 8,400 and 17,200 respectively. (Total global emissions for 2004 were estimated at over 27,200 Mt).
In addition, natural gas itself is a greenhouse gas far more potent than carbon dioxide when released into the atmosphere but is not of major concern due to the small amounts in which this occurs. Natural gas is generally comprised of methane, which has a radioactive forcing twenty times greater than carbon dioxide. This means, however, a ton of methane in the atmosphere traps in as much radiation as 20 tons of carbon dioxide. Carbon dioxide still receives the lion's share of attention over greenhouse gases because it is in much higher concentration.

3.9.2 Pollutants

Natural gas produces far lower amounts of sulphur dioxide and nitrous oxides than any other fossil fuel.

3.10 Safety

In any form, a minute amount of odourant such as t-butyl mercaptan, with a rotting-cabbage-like smell, is added to the otherwise colourless and almost odourless gas, so that leaks can be detected before a fire or explosion occurs. Sometimes a related compound, thiophane is used, with a rotten-egg smell. Adding odourant to natural gas began in the United States after the 1937 New London School explosion. The buildup of gas in the school went unnoticed, killing three hundred students in a faculty when it ignited. Odourants are considered non-toxic in the extremely low concentrations occurring in natural gas delivered to the end user.

In mines, where methane seeping from rock formations has no odour, sensors are used, and mining apparatus have been specifically developed to avoid ignition sources, e.g., the Davy lamp.

Explosions caused by natural gas leaks occur a few times each year. Individual homes, small businesses and boats are most frequently affected when an internal leak builds up gas inside the structure. Frequently, the blast will be enough to significantly damage a building but leave it standing. In these cases, the people inside tend to have minor to moderate injuries. Occasionally, the gas can collect in high enough quantities to cause a deadly explosion, disintegrating one or more buildings in the process. The gas usually dissipates readily outdoors, but can sometimes collect in dangerous quantities if weather conditions are right. However, considering the tens of millions of structures that use the fuel, the individual risk of using natural gas is very low.

Some gas fields yield sour gas containing hydrogen sulphide (H_2S). This untreated gas is toxic. Amine gas treating which is an industrial scale process to remove acidic gaseous components is often used to remove hydrogen sulphide from natural gas.

Extraction of natural gas (or oil) leads to decrease in pressure in the reservoir. This in turn may lead to subsidence at ground level. Subsidence may affect ecosystems, waterways, sewer and water supply systems, foundations, etc.

Natural gas heating systems are a minor source of carbon monoxide deaths in the United States. According to the US Consumer Product Safety Commission (2008), 56% of unintentional deaths from non-fire CO poisoning were associated with engine-driven tools like gas-powered generators and lawn mowers. Natural gas heating systems accounted for 4% of these deaths. Improvements in natural gas furnace designs have greatly reduced CO poisoning concerns. Detectors are also available that warn of carbon monoxide and/or explosive gas (methane, propane, etc.).

3.10.1 Energy Content, Statistics and Pricing

Quantities of natural gas are measured in normal cubic meters (corresponding to 0°C at 101.325 kPa) or in standard cubic feet (corresponding to 60 °F (16 °C) and 14.73 psi). The gross heat of combustion of one normal cubic meter of commercial quality natural gas is around 39 megajoules (≈10.8 kWh), but this can vary by several per cent.

The price of natural gas varies greatly depending on location and type of consumer. In 2007, a price of $7 per 1,000 cubic feet (28 m^3) was typical in the United States. The typical caloric value of natural gas is roughly 1,000 British Thermal Units (BTU) per cubic foot, depending on gas composition. This corresponds to around $7 per million BTU, or around $7 per gigajoule. In April 2008, the wholesale price was $10 per 1,000 cubic feet (28 m^3) ($10/MMBTU). The residential price varies from 50 to 300 % more than the wholesale price. At the end of 2007, this was $12-$16 per 1,000 cu ft (28 m^3). Natural gas in the United States is traded as a futures contract on the New York Mercantile Exchange. Each contract is for 10,000 MMBTU (gigajoules), or 10 billion BTU. Thus, if the price of gas is $10 per million BTUs on the NYMEX, the contract is worth $100,000.

Natural gas is also traded as a commodity in Europe, principally at the United Kingdom NBP and related European hubs, such as the TTF in the Netherlands. In US units, one standard cubic foot of natural gas produces around 1,028 British Thermal Units (BTU). The actual heating value when the water formed does not condense is the net heat of combustion and can be as much as 10% less.

In the United States, retail sales are often in units of therms (th); 1 therm = 100,000 BTU. Gas meters measure the volume of gas used, and this is converted to therms by multiplying the volume by the energy content of the gas used during that period, which varies slightly over time. Wholesale transactions are generally done in decatherms (Dth), or in thousand decatherms (MDth), or in million decatherms (MMDth). A million decatherms is roughly a billion cubic feet of natural gas.

In the rest of the world, LNG (liquified natural gas) and LPG (liquified petroleum gas) is traded in metric tons or mmBTU as spot deliveries. Long term contracts are signed in metric tons. The LNG and LPG are transported by specialised transport ships, as the gas is liquified at cryogenic temperatures. The specification of each LNG/LPG cargo will usually contain the energy content, but this information is in general not available to the public.

SELF ASSESSMENT EXERCISE 2

1. What is biogas?
2. What is the meaning of BTU?
3. Why is LPG the dominant source of rural gas over CNG?

4.0 CONCLUSION

Photosynthesis is the basis for mass production of organic matter. About 2 billion years ago in the Precambrian, photosynthesis emerged as a worldwide phenomenon thus laying the foundation for the food chain and the evolution of higher forms of life. With the emergence of photosynthesis the atmospheric oxygen was enrich which also lead to the mass production of organic matter.

The deposition of sediments rich in organic matter, i.e., such as contain more than about 0.5% by weight or organic carbon, is restricted to certain boundary conditions. Such sediments are deposited in aquatic environments receiving a certain minimum amount of organic matter.

5.0 SUMMARY

The origin, accumulation and migration of natural gas were examined in this unit. The difference between natural gas and other gases, processing of natural gas and uses was also examined. Problems associated with the storage and transportation of natural gas as a result of its low density was also discussed. In addition, the environmental effect, energy content, statistics and pricing was also examined.

6.0 TUTOR-MARKED ASSIGNMENT

1. Accumulation of gas can be conventional or unconventional discuss?
2. What are the problems associated with the storage and transportation of the various gas product?
3. Tertiary butyl mercaptan (tert-butyl mercaptan) and related compounds such as thiophene are added to gas why?
4. Discuss briefly the various uses of natural gas.

7.0 REFERENCES/FURTHER READING

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Benefits of Integrating NGL Extraction and LNG Liquefaction

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UNIT 4 OIL WELL, OIL FIELD AND RESERVOIR

CONTENTS

1.0 INTRODUCTION

An oil well is a general term for any boring through the earth’s surface that is designed to find and produce petroleum oil. Usually some natural gas is produced along with the oil. A well designed to produce mainly or only gas may be termed a gas well. Thus, in this unit we will examine what an oil well is, different types of well, and various terms associated with oil well such as completion, production, and abandonment. Reservoir, traps including different types of trap and estimation of reservoir will also be considered.

2.0 OBJECTIVES

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

- describe an oil field
- define an oil well and the various terms associated with oil well such as completion, production, and abandonment
- state the different types of well

explain what is meant by reservoir in petroleum chemistry
define traps and enumerate different types of traps
discuss an estimation of a reservoir.

3.0 MAIN CONTENT

3.1 Oil Field

Oil field is a region with an abundance of oil wells extracting petroleum (crude oil) from below ground. Because the oil reservoirs typically extend over a large area, possibly several hundred kilometres across, full exploitation entails multiple wells scattered across the area. In addition, there may be exploratory wells probing the edges, pipelines to transport the oil elsewhere, and support facilities. Because an oil field may be remote from civilisation, establishing a field is often an extremely complicated exercise in logistics. For instance, workers have to work there for months or years and require housing. In turn, housing and equipment require electricity and water. Pipelines in cold areas may need to be heated. Excess natural gas needs to be burned off if there is no way to make use of it, requiring a furnace and stacks, and pipes to carry it from well to furnace.

Thus, the typical oil field resembles a small self-contained city in the midst of a landscape dotted with drilling rigs and/or the pump jacks known as "nodding donkeys" because of their bobbing arm. Several companies, such as BJ Services, Bechtel, Esso, Schlumberger Limited, Baker Hughes and Halliburton, have organisations that specialise in the large-scale construction of the infrastructure and providing specialised services required to operate a field profitably.

More than 40,000 oil fields are scattered around the globe, on land and offshore. The largest are the Ghawar Field in Saudi Arabia and the Burgan Field in Kuwait, with more than 60 billion barrels (9.5×10^9 m^3) estimated in each. Most oil fields are much smaller. According to the US Department of Energy (Energy Information Administration), as of 2003 the US alone had over 30,000 oil fields.

In the modern age, the location of oil fields with proven oil reserves is a key underlying factor in many geopolitical conflicts. The term oil field is also used as shorthand to refer to the entire petroleum industry.

3.2 Oil Well

An oil well is a general term for any boring through the earth’s surface that is designed to find and produce petroleum oil hydrocarbons. Usually some natural gas is produced along with the oil. A well designed to produce mainly or only gas may be termed a gas well.

The well is created by drilling a hole of about 5 to 36 inches (127.0 mm to 914.4 mm) diameter into the earth with a drilling rig which rotates a drill string with a bit attached. After the hole is drilled, sections of steel pipe (casing), slightly smaller in diameter than the borehole, are placed in the hole. Cement may be placed between the outside of the casing and the borehole. The casing provides structural integrity to the newly drilled wellbore in addition to isolating potentially dangerous high pressure zones from each other and from the surface.

With these zones safely isolated and the formation protected by the casing, the well can be drilled deeper (into potentially more-unstable and violent formations) with a smaller bit, and also cased with a smaller size casing. Modern wells often have 2–5 sets of subsequently smaller hole sizes drilled inside one another, each cemented with casing.

To drill the well:

> The drill bit, aided by the weight of thick walled pipes called “drill collars” above it, cuts into the rock. There are different types of drillbit, some cause the rock to fail by compressive failure. Others shear slices off the rock as the bit turns.
>
> Drilling fluid (mud) is pumped down the inside of the drill pipe and exits at the drill bit. Drilling mud is a complex mixture of fluids, solids and chemicals which must be carefully tailored to provide the correct physical and chemical characteristics required to safely drill the well. Particular functions of the drilling mud include cooling the bit, lifting rock cuttings to the surface, preventing destabilisation of the rock in the wellbore walls and overcoming the pressure of fluids inside the rock so that these fluids don’t enter the wellbore.
>
> The generated rock “cuttings” are swept up by the drilling fluid as it circulates back to surface outside the drill pipe. The fluid then goes through “shakers” which strain the cuttings from the good fluid which is returned to the pit. Watching for abnormalities in the returning cuttings and monitoring pit volume or rate of returning fluid are imperative to catch “kicks” (when the formation pressure at the depth of the bit is more than the hydrostatic head of the mud above, which if not controlled temporarily by closing the blowout preventers and ultimately by increasing the density of the drilling fluid would allow formation fluids and mud to come up uncontrollably) early.
>
> The pipe or drill string to which the bit is attached is gradually lengthened as the well gets deeper by screwing in additional 30-

foot (10 m) joints (i.e., sections) of pipe under the kelly or top drive at the surface. This process is called making a connection. Usually joints are combined into 3 joints equaling 1 stand. Some smaller rigs only use 2 joints and some rigs can handle stands of 4 joints.

This process is all facilitated by a drilling rig which contains all necessary equipment to circulate the drilling fluid, hoist and turn the pipe, control down hole pressures, remove cuttings from the drilling fluid, and generate onsite power for these operations.

3.2.1 Completion

After drilling and casing the well, it must be 'completed'. Completion is the process in which the well is enabled to produce oil or gas.

In a cased-hole completion, small holes called perforations are made in the portion of the casing which passed through the production zone, to provide a path for the oil to flow from the surrounding rock into the production tubing. In open hole completion, often 'sand screens' or a 'gravel pack' is installed in the last drilled, uncased reservoir section. These maintain structural integrity of the wellbore in the absence of casing, while still allowing flow from the reservoir into the wellbore. Screens also control the migration of formation sands into production tubulars and surface equipment, which can cause washouts and other problems, particularly from unconsolidated sand formations in offshore fields.

After a flow path is made, acids and fracturing fluids are pumped into the well to fracture, clean, or otherwise prepare and stimulate the reservoir rock to optimally produce hydrocarbons into the wellbore. Finally, the area above the reservoir section of the well is packed off inside the casing, and connected to the surface via a smaller diameter pipe called tubing. This arrangement provides a redundant barrier to leaks of hydrocarbons as well as allowing damaged sections to be replaced. Also, the smaller diameter of the tubing produces hydrocarbons at an increased velocity in order to overcome the hydrostatic effects of heavy fluids such as water.

In many wells, the natural pressure of the subsurface reservoir is high enough for the oil or gas to flow to the surface. However, this is not always the case, especially in depleted fields where the pressures have been lowered by other producing wells, or in low permeability oil reservoirs. Installing smaller diameter tubing may be enough to help the production, but artificial lift methods may also be needed. Common solutions include down hole pumps, gas lift, or surface pump jacks.

Many new systems in the last ten years have been introduced for well completion. Multiple packer systems with frac ports or port collars in an all in one system have cut completion costs and improved production, especially in the case of horizontal wells. These new systems allow casings to run into the lateral zone with proper packer/frac port placement for optimal hydrocarbon recovery.

SELF ASSESSMENT EXERCISE 1

1. Define oil field.
2. What do you understand by completion?
3. Define / explain what is meant by production tree.
4. What are oil wells?
5. What is the importance of casing in drilling of bore well?

3.2.2 Production

The production stage is the most important stage of a well's life, when the oil and gas are produced. By this time, the oil rigs and work over rigs used to drill and complete the well have moved off the wellbore, and the top is usually outfitted with a collection of valves called a production tree. These valves regulate pressures, control flows, and allow access to the wellbore in case further completion work is needed. From the outlet valve of the production tree, the flow can be connected to a distribution network of pipelines and tanks to supply the product to refineries, natural gas compressor stations, or oil export terminals.

As long as the pressure in the reservoir remains high enough, the production tree is all that is required to produce the well. If the pressure depletes and it is considered economically viable, an artificial lift method mentioned in the completions section can be employed.

Workovers are often necessary in older wells, which may need smaller diameter tubing, scale or paraffin removal, acid matrix jobs, or completing new zones of interest in a shallower reservoir. Such remedial work can be performed using workover rigs – also known as *pulling units* or *completion rigs* – to pull and replace tubing, or by the use of well intervention techniques utilising coiled tubing. Depending on the type of lift system and wellhead a rod rig or flushby can be used to change a pump without pulling the tubing.

Enhanced recovery methods such as water flooding, steam flooding, or CO_2 flooding may be used to increase reservoir pressure and provide a “sweep” effect to push hydrocarbons out of the reservoir. Such methods require the use of injection wells (often chosen from old production wells in a carefully determined pattern), and are used when facing problems with reservoir pressure depletion, high oil viscosity, or can even be employed early in a field's life. In certain cases, depending on the reservoir’s geomechanics, reservoir engineers may determine that ultimate recoverable oil may be increased by applying a water flooding strategy early in the field's development rather than later. Such enhanced recovery techniques are often called “tertiary recovery”.

3.2.3 Abandonment

As a well ages and the reservoir is depleted, the oil produced begins to fall. The production rate at which the well's revenue is so low that it no longer makes a profit is called the "economic limit." The equation to determine the economic limit includes taxes, operating cost, oil price, and royalty. When oil taxes are raised, the economic limit is raised. When oil price is increased, the economic limit is lowered. When the economic limit is raised, the life of the well is shortened and proven oil reserves are lost. Conversely, when the economic limit is lowered, the life of the well is lengthened.

When the economic limit is reached, the well becomes a liability and it is abandoned. In this process, tubing is removed from the well and sections of well bore are filled with cement to isolate the flow path between gas and water zones from each other, as well as the surface. Completely filling the well bore with cement is costly and unnecessary. The surface around the wellhead is then excavated, and the wellhead and casing are cut off, a cap is welded in place and then buried.

At the economic limit, there often is still a significant amount of unrecoverable oil left in the reservoir. It might be tempting to defer physical abandonment for an extended period of time; hoping that the oil price will go up or those new supplemental recovery technique will be perfected. However, lease provisions and governmental regulations usually require quick abandonment, liability and tax concerns also may favour abandonment.

In theory, an abandoned well can be reentered and restored to production (or converted to injection service for supplemental recovery or for downhole hydrocarbons storage), but reentry often proves to be difficult mechanically and not cost effective.

3.2.4 Types of Wells

Oil wells come in many varieties. There can be wells that produce oil, wells that produce oil *and* natural gas, or wells that *only* produce natural gas. Natural gas is almost always a by-product of producing oil, since the small, light gas carbon chains come out of solution as it undergoes pressure reduction from the reservoir to the surface, similar to uncapping a bottle of soda pop where the carbon dioxide effervesces. Unwanted natural gas can be a disposal problem at the well site. If there is not a market for natural gas near the wellhead it is virtually valueless since it must be piped to the end user. Until recently, such unwanted gas was burned off at the well site, but due to environmental concerns this practice is becoming less common. Often, unwanted (or 'stranded' gas without a market) gas is pumped back into the reservoir with an 'injection' well for disposal or repressurising the producing formation. Another solution is to export the natural gas as a liquid. Gas-to-Liquid, (GTL) is a developing technology that converts stranded natural gas into synthetic gasoline, diesel or jet fuel through the Fischer-Tropsch process. Such fuels can be transported through conventional pipelines and tankers to users. Proponents claim GTL fuels burn cleaner than comparable petroleum fuels. Another obvious way to classify oil wells is by land or offshore wells. There is very little difference in the well itself. An offshore well targets a reservoir that happens to be underneath an ocean. Due to logistics, drilling an offshore well is far more costly than an onshore well. By far the most common type is the onshore well.

Another way to classify oil wells is by their purpose in contributing to the development of a resource. They can be characterised as:

> *production wells* are drilled primarily for producing oil or gas, once the producing structure and characteristics are determined
> *appraisal wells* are used to assess characteristics (such as flow rate) of a proven hydrocarbon accumulation
> *exploration wells* are drilled purely for exploratory (information gathering) purposes in a new area
> *wildcat wells* are those drilled outside of and not in the vicinity of known oil or gas fields.

At a producing well site, active wells may be further categorised as:

> *oil producers,* producing predominantly liquid hydrocarbons, but mostly with some associated gas.
> *gas producers,* producing almost entirely gaseous hydrocarbons.
> *water injectors,* injecting water into the formation to maintain reservoir pressure or simply to dispose of water produced with the hydrocarbons because even after treatment, it would be too oily and too saline to be considered clean for dumping overboard, let alone into a fresh water source, in the case of onshore wells. Frequently water injection has an element of reservoir management and produced water disposal.
> *aquifer producers,* intentionally producing reservoir water for re-injection to manage pressure. This is in effect moving reservoir

water from where it is not as useful to where it is more useful. These wells will generally only be used if produced water from the oil or gas producers is insufficient for reservoir management purposes. Using aquifer produced water rather than sea water is due to the chemistry.

gas injectors, injecting gas into the reservoir often as a means of disposal or sequestering for later production, but also to maintain reservoir pressure.

Lahee classification

New Field Wildcat (NFW) – far from other producing fields and on a structure that has not previously produced.

New Pool Wildcat (NPW) – new pools on already producing structure.

Deeper Pool Test (DPT) – on already producing structure and pool, but on a deeper pay zone.

Shallower Pool Test (SPT) – on already producing structure and pool, but on a shallower pay zone.

Outpost (OUT) – usually two or more locations from nearest productive area.

Development Well (DEV) – can be on the extension of a pay zone, or between existing wells (*Infill*).

3.3 Oil Reservoir

A petroleum reservoir or an oil and gas reservoir is a subsurface pool of hydrocarbons contained in porous or fractured rock formations. The naturally occurring hydrocarbons are trapped by overlying rock formations with lower permeability.

Once a source rock generates and expels petroleum, the petroleum migrates from the source rock to a rock that can store the petroleum. A rock capable of storing petroleum in its pore spaces, the void spaces between the grains of sediment in a rock, is known as a reservoir rock. Rocks that have sufficient pore space through which petroleum can move include sandstone, limestone, and rocks that have many fractures. A good reservoir rock might have pore space that exceeds 30% of the rock volume. Poor quality reservoir rocks have less than 10% void space capable of storing petroleum. Rocks that lack pore space tend to lack permeability, the property of rock that allows fluid to pass through the pore spaces of the rock. With very few pores, it is not likely that the pores are connected and less likely that fluid will flow through the rock than in a rock with larger or more abundant pore spaces. Highly porous rocks tend to have better permeability because of the greater number of pores and larger pore sizes that tend to allow fluids to move through the reservoir more easily. The property of permeability is critical to producing petroleum: If fluids cannot migrate through a reservoir rock to a petroleum production well, the well will not produce much petroleum and the money spent to drill the well has been wasted.

In order for a reservoir to contain petroleum, the reservoir must be shaped and sealed like a container. Good petroleum reservoirs are sealed by a less porous and permeable rock known as a seal or cap rock. The seal prevents the petroleum from migrating further. Rocks like shale and salt provide excellent seals for reservoir rocks because they do not allow fluids to pass through them easily. Seal-forming rocks tend to be made of small particles of sediment that fit closely together so that pore spaces are small and poorly connected. The permeability of a seal must be virtually zero in order to retain petroleum in a reservoir rock for millions to hundreds of millions of years, the time span between formation of petroleum to the discovery and production of many petroleum fields. Likewise, the seal must not be subject to forces within the earth that might cause fractures or other breaks in the seal to form.

Reservoir rocks and seals work together to form a trap for petroleum. Typical traps for petroleum include hills shaped like upside-down bowls below the surface of the earth, known as anticlines, or traps formed by faults. Abrupt changes in rock type can form good traps, such as sandstone deposits next to shale deposits, especially if a sand deposit is encased in a rock that is sufficiently rich in organic matter to act as a petroleum source and endowed with the properties of a good seal. An important aspect of the formation of petroleum accumulations is timing. The reservoir must have been deposited prior to petroleum migrating from the source rock to the reservoir rock. The seal and trap must have been developed prior to petroleum accumulating in the reservoir, or else the petroleum would have migrated farther. The source rock must have been exposed to the appropriate temperature and pressure conditions over long periods of time to change the organic matter to petroleum. The necessary coincidence of several conditions is difficult to achieve in nature.

Petroleum is typically found beneath the surface of the earth in accumulations known as fields. Fields can contain oil, gas, tar, water, and other substances, but oil, gas, and water are the most common. In order for a field to form, there must be some sort of structure to trap the petroleum, a seal on the trap that prohibits leakage of the petroleum, and a reservoir rock that has adequate pore space, or void space, to hold the petroleum.

To find these features together in an area in which petroleum has been generated by chemical reactions affecting organic remains requires many coincidences of timing of natural processes. Rocks occur in many environments, including lakes, deep areas of the seas and oceans, and swamps. The source rocks must be buried deep enough below the surface of the earth to heat up the organic material, but not so deep that the rocks metamorphose or that the organic material changes to graphite or materials other than hydrocarbons. Temperatures less than 302° F (150°C) are typical for petroleum generation.

3.3.1 Traps

The traps required in the last step of the reservoir formation process have been classified by petroleum geologists into two types: **structural** and **stratigraphic**. A reservoir can be formed by one kind of trap or a combination of both.

3.3.2 Structural Traps

Structural traps are formed by a deformation in the rock layer that contains the hydrocarbons. Domes, anticlines, and folds are common structures. Fault-related features also may be classified as structural traps if closure is present. Structural traps are the easiest to locate by surface and subsurface geological and geophysical studies. They are the most numerous among traps and have received a greater amount of attention in the search for oil than all other types of traps. An example of this kind of trap starts when salt is deposited by shallow seas. Later, a sinking seafloor deposits organic-rich shale over the salt, which is in turn covered with layers of sandstone and shale. Deeply buried salt tends to rise unevenly in swells or salt domes, and any oil generated within the sediments is trapped where the sandstones are pushed up over or adjacent to the salt dome.

3.3.3 Stratigraphic Traps

Stratigraphic traps are formed when other beds seal a reservoir bed or when the permeability changes (facies change) within the reservoir bed itself. Stratigraphic traps can form against either younger or older time surfaces.

3.4 Estimating Reserves

After the discovery of a reservoir, a programme of appraisal will seek to build a better picture of the accumulation. In the simple text book example of a uniform reservoir, the first stage is to use seismic to determine the possible size of the trap. Appraisal wells can be used to determine the location of oil-water contact and with it, the height of the oil-bearing sands. Often coupled with seismic data, it is possible to estimate the volume of oil bearing reservoir. The next step is to use information from appraisal wells to estimate the porosity of the rock. This is commonly 20-35% or less (the percentage of the total volume that contains fluids rather than solid rock). This can give a picture of the actual capacity. Laboratory testing can determine the characteristics of the reservoir fluids, particularly the expansion factor of the oil (how much the oil will expand when brought from the high pressure, high temperature environment of the reservoir to "stock tank" conditions at the surface.

With this knowledge, it is then possible to estimate how many “stock tank” barrels of oil are located in the reservoir. This is called the Stock Tank Oil Initially In Place (STOIIP). As a result of studying properties such as the permeability of the rock (how easily fluids can flow through the rock) and possible drive mechanisms, it is possible to then estimate the recovery factor (what proportion of the oil in place can be reasonably expected to be produced). This is commonly between 30-35%. This finally gives a value for the recoverable reserves. The difficulty in practice is that reservoirs are not uniform. They have a variable porosities and permeabilities and may be compartmentalised, with fractures and faults breaking them up and complicating fluid flow.

3.5 Production

To obtain the contents of the oil reservoir, it is usually necessary to drill into the Earth's crust, although surface oil seeps exist in some parts of the world. A virgin reservoir may be under sufficient pressure to initially push hydrocarbons to surface. However, as the fluids are produced, the pressure will often decline, and production will falter with it. However, the reservoir may respond to fluid withdrawal in a way that will tend to maintain the pressure. Artificial drive methods may be necessary. This mechanism (also known as depletion drive) depends on the associated gas of the oil. The virgin reservoir may be entirely liquid, but will be expected to have gaseous hydrocarbons in solution due to the pressure. As the reservoir depletes, the pressure falls below the bubble point and the gas comes out of solution to form a gas cap at the top. This gas cap pushes down on the liquid helping to maintain pressure.

In reservoirs already having a gas cap (the virgin pressure is already below bubble point), the gas cap expands with the depletion of the reservoir, pushing down on the liquid sections applying extra pressure.

Below the hydrocarbons may be a ground water aquifer. Water, as with all liquids, is compressible to a small degree. As the hydrocarbons are depleted, the reduction in pressure in the reservoir causes the water to expand slightly. Although this expansion is minute, if the aquifer is large enough, this will translate into a large increase in volume, which will push up on the hydrocarbons, maintaining pressure. If the natural drives are insufficient, as they very often are, then the pressure can be artificially maintained by injecting water into the aquifer or gas into the gas cap.

3.6 Oil in Place

Oil in place is the total hydrocarbon content of an oil reservoir and is often abbreviated STOOIP, which stands for Stock Tank Original Oil In Place, or STOIIP for Stock Tank Oil Initially In Place, referring to the oil in place before the commencement of production. In this case, *stock tank* refers to the storage vessel (often purely notional) containing the oil after production.

Oil in place must not be confused with oil reserves that are the technically and economically recoverable portion of oil volume in the reservoir. Current recovery factors for oil fields around the world typically range between 10 and 60%; some are over 80%. The wide variance is due largely to the diversity of fluid and reservoir characteristics for different deposits. Accurate calculation of the value of STOOIP requires knowledge of:

volume of rock containing oil (bulk rock volume, in the USA this is usually in acre-feet)
percentage porosity of the rock in the reservoir
percentage water content of that porosity
amount of shrinkage that the oil undergoes when brought to the earth's surface
and is achieved using the formula

$$N = \frac{7758\, V_b\, \phi\, (1 - S_w)}{B_{oi}} \quad \text{[stb]}$$

Or

$$N = \frac{V_b\, \phi\, (1 - S_w)}{B_{oi}} \quad [\text{m}^3]$$

Where

N = STOIIP (barrels)
V_b = Bulk (rock) volume (acre-feet or cubic metres)
ϕ = Fluid-filled porosity of the rock (fraction)
S_w = Water saturation - water-filled portion of this porosity (fraction)

B_{oi} = Formation volume factor (dimensionless factor for the change in volume between reservoir and standard conditions at surface)

Gas saturation S_g is traditionally omitted from this equation.

The constant value 7758 converts acre-feet to stock tank barrels. An acre of reservoir 1 foot thick would contain 7758 barrels of oil in the limiting case of 100% porosity, zero water saturation and no oil shrinkage. If the metric system is being used, a conversion factor of 6.289808 can be used to convert cubic metres to stock tank barrels. A one-cubic metre container would hold 6.289808 barrels of oil.

3.7 Formation Volume Factor

When oil is produced, the high reservoir temperature and pressure decreases to surface conditions and gas bubbles out of the oil. As the gas bubbles out of the oil, the volume of the oil decreases. Stabilised oil under surface conditions (either 60^o F and 14.7 psi or 15^o C and 101.325 kPa) is called stock tank oil. Oil reserves are calculated in terms of stock tank oil volumes rather than reservoir oil volumes. The ratio of stock tank volume to oil volume under reservoir conditions is called the formation volume factor (FVF). It usually varies from 1.0 to 1.7. A formation volume factor of 1.4 is characteristic of high-shrinkage oil and 1.2 of low-shrinkage oil.

3.8 Reservoir Engineering

Reservoir engineering is a branch of petroleum engineering, which applies scientific principles to the drainage problems arising during the development and production of oil and gas reservoirs so as to obtain a high economic recovery. The working tools of the reservoir engineer are subsurface geology, applied mathematics, and the basic laws of physics and chemistry governing the behaviour of liquid and vapor phases of crude oil, natural gas, and water in reservoir rock.

Of particular interest to reservoir engineers is generating accurate reserves estimates for use in financial reporting to the SEC and other regulatory bodies. Other job responsibilities include numerical reservoir modeling, production forecasting, well testing, well drilling and workover planning, economic modeling, and PVT analysis of reservoir fluids.

Reservoir engineers also play a central role in field development planning, recommending appropriate and cost effective reservoir depletion schemes such as water flooding or gas injection to maximize hydrocarbon recovery.

Reservoir engineers often specialise in two areas:

Surveillance (or production) engineering, i.e. monitoring of existing fields and optimisation of production and injection rates. Surveillance engineers typically use analytical and empirical techniques to perform their work, including decline curve analysis, material balance modeling, and inflow/outflow analysis.
Simulation modeling, i.e. the conduct of reservoir simulation studies to determine optimal development plans for oil and gas reservoirs.

SELF ASSESSMENT EXERCISE 2

1. Mention the two types of traps that you know.
2. What is the full meaning of STOOIP?
3. Define oil reservoir.
4. What is responsible for the deviation of well from true vertical position?
5. What are the two areas of specialisation of reservoir engineers?

4.0 CONCLUSION

In this unit, we have been able to know that oil and natural gas are produced by the same geological process by anaerobic digestion / decay of organic matter deep under the earth's surface. As a consequence, oil and natural gas are often found together. Because both oil and natural gas are lighter than water, they tend to rise from their sources until they either seep to the surface or are trapped by a non-permeable layer of rock. Like oil, natural gas is often found underwater in offshore gas fields.

In addition, we have also been able to know that 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.

5.0 SUMMARY

In this unit, you have learnt that:

Oil field is a region with an abundance of oil wells extracting petroleum (crude oil) from below ground.
An oil well is a general term for any boring through the earth's surface that is designed to find and produce petroleum oil (crude

oil). Usually some natural gas is produced along with the oil. A well designed to produce mainly gas may be termed gas well.

A petroleum reservoir or an oil and gas reservoir is a subsurface pool of hydrocarbons contained in porous or fractured rock formations.

Oil in place is the total hydrocarbon content of an oil reservoir known as Stock Tank Original Oil In Place and is often abbreviated STOOIP.

Reservoir engineering is a branch of petroleum engineering, which applies scientific principles to the drainage problems arising during the development and production of oil and gas reservoirs so as to obtain a high economic recovery.

6.0 TUTOR-MARKED ASSIGNMENT

1. Briefly discuss stock tank oil
2. How will you estimate how many stock tank barrels of oil located in a reservoir?
3. Discuss in details Oil in Place.
4. Explain the usefulness of a gas cap reservoir.
5. What are the attributes of a good reservoir?
6. There are different ways of classifying a well. Discuss the classification based on their purpose in contributing to developing a resource.
7. What are the problems associated with establishing a field?

7.0 REFERENCES/FURTHER READING

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MODULE 2 COMPOSITION OF CRUDE OIL AND NATURAL GAS

Unit 1 Composition, Properties and Classification of Crude Oil
Unit 2 Natural Gas Origin, Transportation and Uses
Unit 3 Basic Petroleum Refining
Unit 4 Natural Gas Treatment Processes

UNIT 1 COMPOSITION, PROPERTIES AND CLASSIFICATION OF CRUDE OIL

CONTENTS

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

By 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

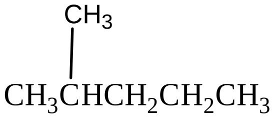
The principal constituents of crude oil are hydrocarbon compounds. All hydrocarbon classes are present in the crude mixture, except alkenes and alkynes. This may indicate that crude oil originated under a reducing atmosphere. The following is a brief description of the different hydrocarbon classes found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

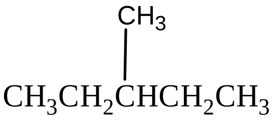
$CH_3(CH_2)_4CH_3$

n-Hexane



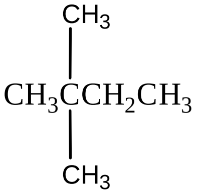
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

2-Methylpentane
isohexane



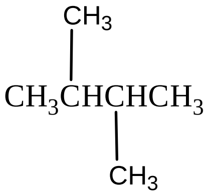
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

3-Methylpentane



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

2,2-dimethylbutane



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

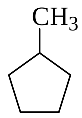
2,3-dimethylbutane

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.

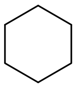
3.2.2 Cycloparaffins (Naphthenic)

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.

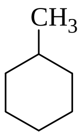
The examples shown here are for three naphthenes of special importance. If a naphtha fraction contains these compounds, the first two can be converted to benzene, and the last compound can dehydrogenate to toluene during processing. Dimethylcyclohexanes are also important precursors for xylenes (see “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



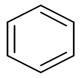
Cyclohexane



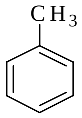
Methylcyclohexane

3.2.3 Aromatic Compounds

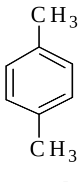
Lower members of aromatic compounds are present in small amounts in crude oil and light petroleum fractions. The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oil. Benzene, 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:



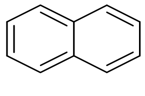
Benzene



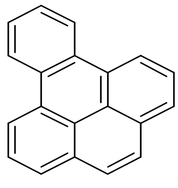
Toluene



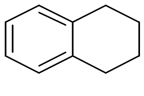
p-Xylene



Naphthalene



1,2-Benzopyrene



Tetralin

SELF ASSESSMENT EXERCISE 1

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.

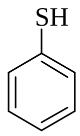
3.2.5 Sulphur Compounds

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:

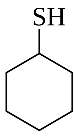
Acidic Sulphur compounds

CH_3SH

Methylmercaptan



Phenylmercaptan



Cyclohexylthiol

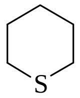
Non -acidic Sulphur compounds

CH_3SCH_3

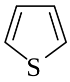
Dimethyl sulphide

$CH_3S\text{-}SCH_3$

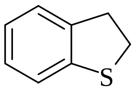
Dimethyldisulphide



Thiocyclohexane



Thiophene

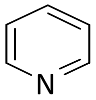


Benzothiophene

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

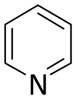
Organic nitrogen compounds occur in crude oil either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin. The nitrogen content in most crude oil is very low and does not exceed 0.1 weight per cent. In some heavy crude, however, the nitrogen 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:

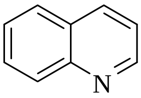


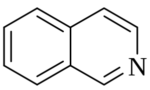
$$+ \ 5H_2 \longrightarrow NH_3 + CH_3CH_2CH_2CH_2CH_3$$

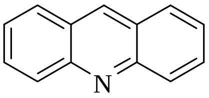
Nitrogen compounds in crude may generally be classified into basic and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure. Both pyridine and pyrrole are stable compounds due to their aromatic nature. The following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

Basic Nitrogen Compounds


Pyridine

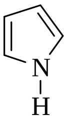

Quinoline

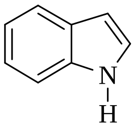

Isoquinoline

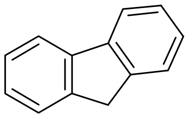

Acridine

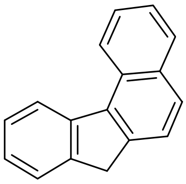
Porphyrins are non-basic nitrogen compounds. The porphyrin ring system is composed of four pyrrole rings joined by =CH-groups. The entire ring system is aromatic. Many metal ions can replace the pyrrole hydrogens and form chelates. The chelate is planar around the metal ion and resonance results in four 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.

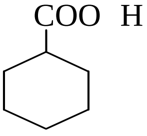
3.2.7 Oxygen Compounds

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:

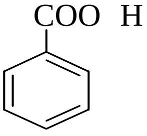
Acidic Oxygen Compounds

$CH_3(CH_2)_nCOOH$

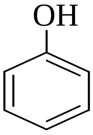
An aliphatic acid



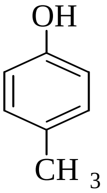
Cyclohexane carboxylic acid



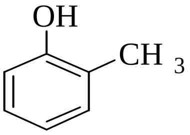
Aromatic acid



Phenol



Para cresylic acid



Ortho cresylic acid

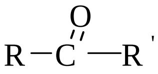
Non-Acidic Oxygen Compounds

$R—COOR'$

Esters

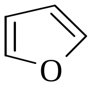
RC ONH R

Amides

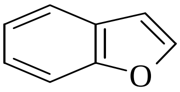


$R-\overset{O}{\overset{\|}{C}}-R'$

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:

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

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

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 2

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 TUTOR-MARKED ASSIGNMENT

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?

7.0 REFERENCES/FURTHER READING

http//www.wikipedia.org

Matar, S. & Hatch, L.F. (1994). *Chemistry of Petrochemical Processes*. (2nd ed.).

UNIT 2 NATURAL GAS ORIGIN, TRANSPORTATION AND USES

CONTENTS

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

By 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.

4.0 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.

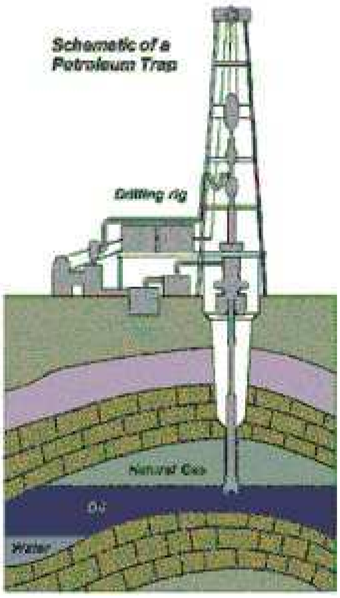


Fig. 1: Schematic Diagram of a Petroleum Trap
(Source: United State Energy Information Administration)

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

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:

a. The reserve may be too remote from a market for natural gas, hence making the construction of pipelines prohibitively expensive.
b. 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 2

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 TUTOR-MARKED ASSIGNMENT

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

CONTENTS

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

By 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.

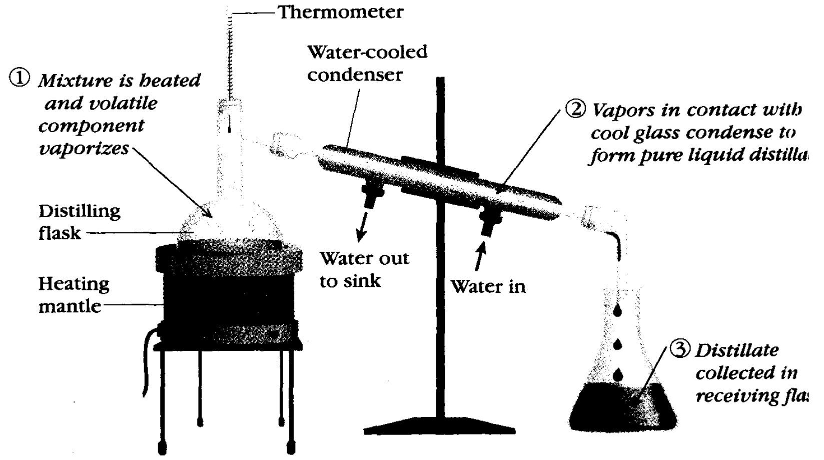

Fig. 1: A Simple Distillation Apparatus
(Source: George H. Schimd Organic Chemistry)

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.

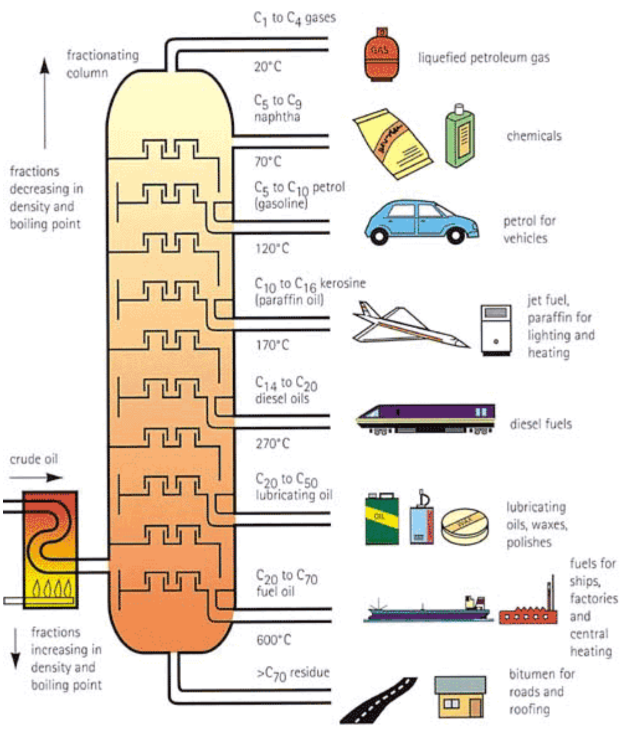

Fig. 2: Fractional Distillation Column
(Diagram by the Institute of Petroleum, UK)

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^{o}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^{o}C; naphtha (no 1 side stream) 95-150^{o}C; kerosene (no 2 side stream) 150 -230^{o}C; and gas oil (no 3 side stream) 230-340^{o}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^{o}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^oC. 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:

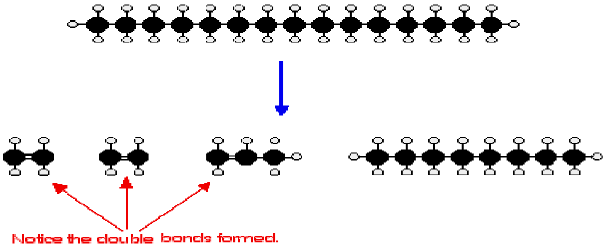

Fig. 3 : Schematic Diagram of Cracking
(*Source*: http//www.wikipedia.org)

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

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^{o}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.

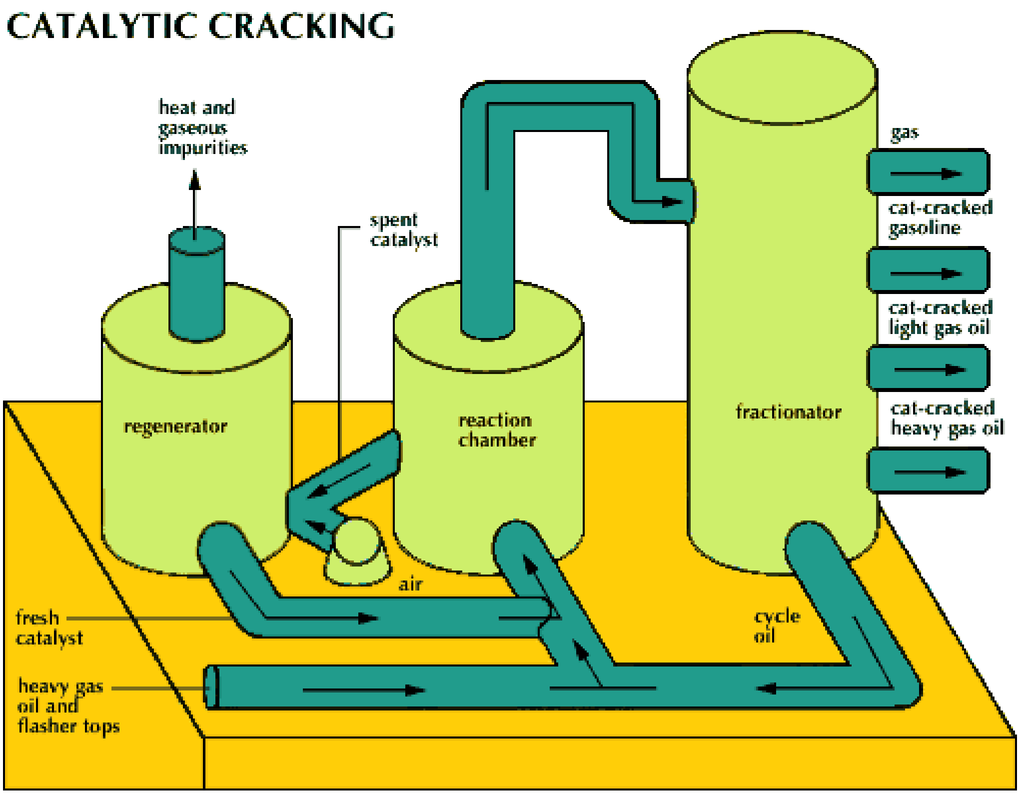

Fig. 4: A Catalytic Cracking Unit
(*Source:* http//www.wikipedia.org)

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*.

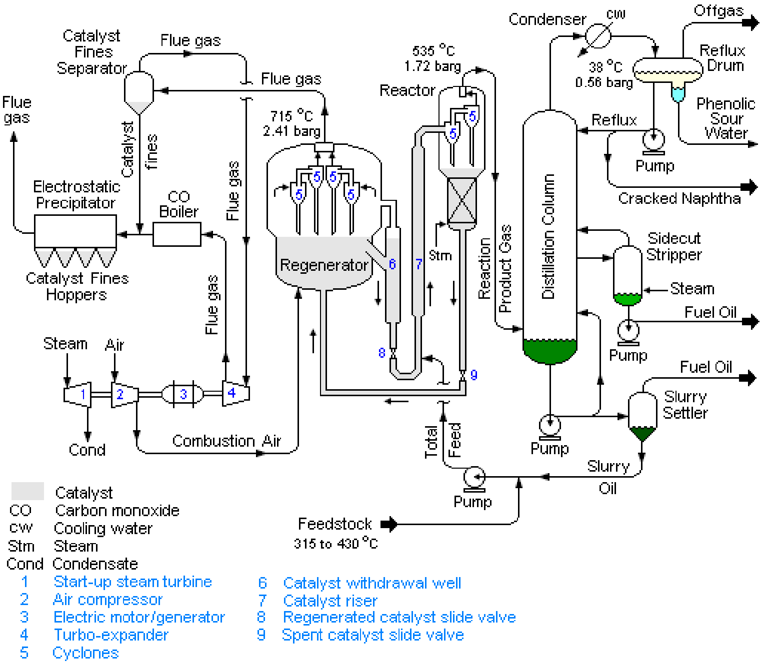

Fig. 5 : A Schematic Flow Diagram of a Fluid Catalytic Cracking Unit as used in Petroleum Refineries
(*Source:* http//www.wikipedia.org)

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 2

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.

7.0 TUTOR-MARKED ASSIGNMENT

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

CONTENTS

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

By 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.

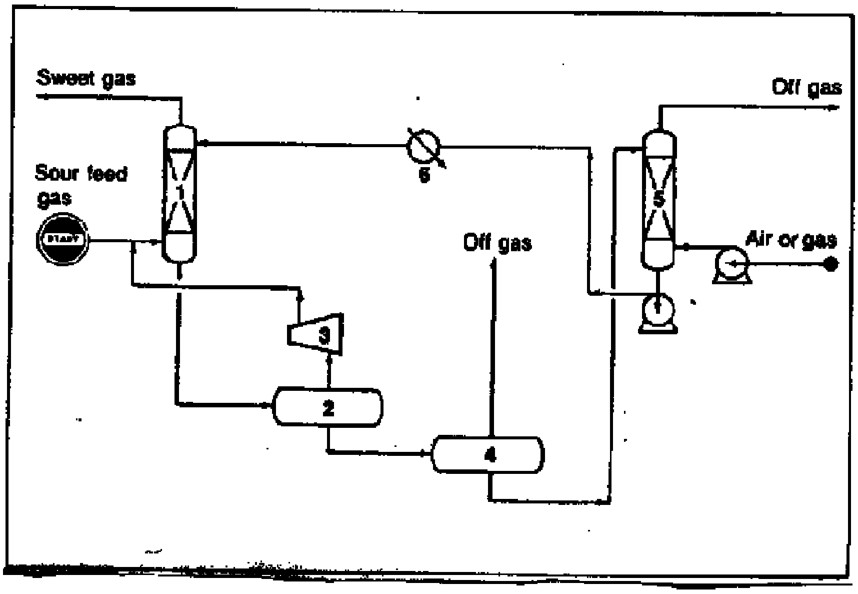

Fig. 1:The Selexol Process for Acid Gas Removal: (1) Absorber, (2) Flash Drum, (3) Compressor, (4) Low-pressure Drum, (5) Stripper, (6) Coole

(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

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 process 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.

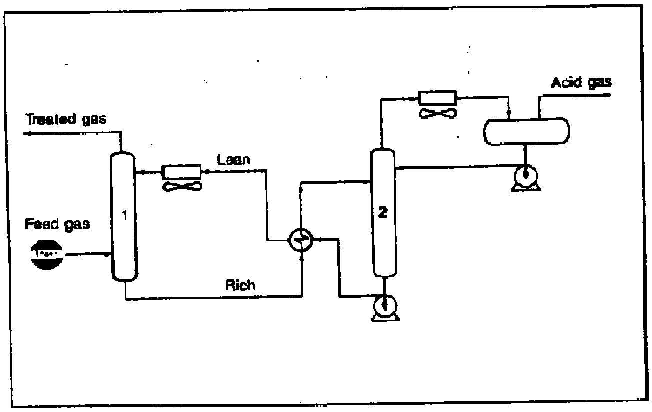

Fig. 2: The Econamine Process: (1) Absorption Tower, (2) Regeneration Tower

(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).

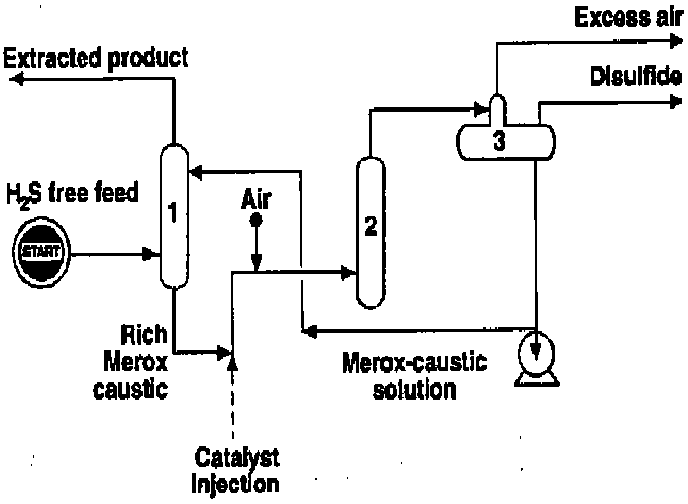

Fig. 3 : The Merox Process: (1) Extractor, (2) Oxidation Reactor
(Source: Chemistry of Petrochemical Processes)

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.

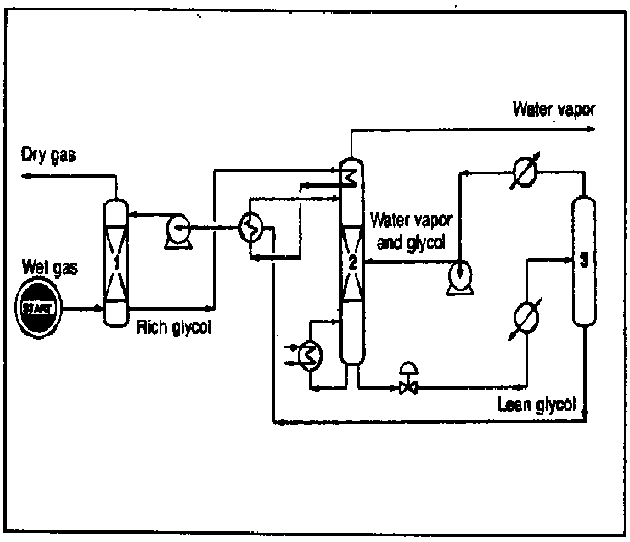

Fig. 4: Flow Diagram of the Dehydrate Process: (1) Absorption Column,
(2) Glycol Sill, (3) Vacuum Drum
(Source: Chemistry of Petrochemical Processes**)**

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, and 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)

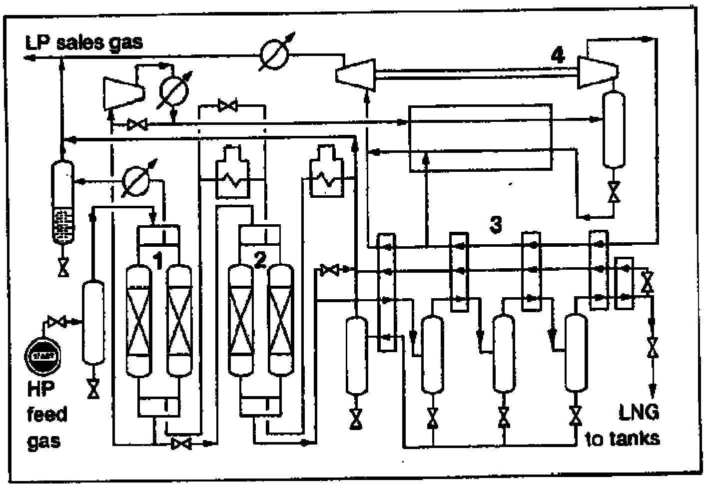

Fig. 5 : Flow Diagram of the Expander Cycle for Liquefying Natural Gas:
(1) Pretreatment (mol.sieve), (2) Heat Exchanger, (3) Turboexpander

(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.

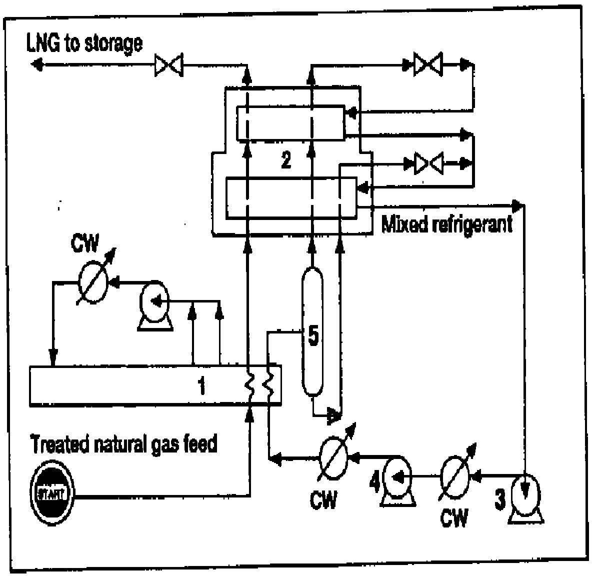

Fig. 6: The MCR Process for Liquefying Natural Gas: (1) Coolers, (2) Heat Exchangers, (3,4) Two Stage Compressors, (5) Liquid-Vapour Phase Separator

(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 2

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

5.0 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.

6.0 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 TUTOR-MARKED ASSIGNMENT

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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MODULE 3 DISTRIBUTION OF PETROLEUM AND NATURAL GAS RESOURCES

UNIT 1 DISTRIBUTION OF NATURAL GASES

CONTENTS

1.0 INTRODUCTION

World natural gas consumption which was about 75 trillion cubic feet (tcf) in 1994 is rising faster than that of any other fossil fuel. The increase is as a result of increase in gas demand for industrial and power generation, in heating of buildings and homes in the design, and operation of gas turbines. This unit shall examine the global distribution, production, consumption and trade in natural gas. Our discussion will also include local distribution, production and consumption, political activities and civil unrest within Nigeria context will also be mentioned.

2.0 OBJECTIVES

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

- explain the world natural gas distribution and production
- describe the world natural gas consumption and trade
- differentiate between upstream and downstream sectors
- discuss political activity and civil unrest
- discuss border disputes
- explain government underfunding.

3.0 MAIN CONTENT

3.1 Petroleum Industry

The petroleum industry is usually divided into three major components: upstream, midstream and downstream. Midstream operations are usually included in the downstream category.

3.1.1 Upstream

The upstream oil sector is a term commonly used to refer to the searching for and the recovery and production of crude oil and natural gas.

The upstream oil sector is also known as the *exploration and production (E&P) sector*. It includes the searching for potential underground or underwater oil and gas fields, drilling of exploratory wells, and subsequently operating the wells that recover and bring the crude oil and/or raw natural gas to the surface.

The upstream oil industry is the single most important sector in the country's economy, providing over 90% of its total exports. Oil is produced from five of Nigeria’s seven sedimentary basins: the Niger Delta, Anambra, Benue Trough, Chad, and Benin. The Niger Delta, the Onshore and Shallow Offshore basins can be considered explored. Ventures here are low risk and the basins contain about 80% of producing wells drilled in Nigeria. During the later 1990s, exploration focus turned to high risk ventures in the frontier basins of the deep water offshore with encouraging success. These ventures are becoming increasingly attractive with developments in deepwater exploration and production technology.

3.1.2 Downstream

The downstream oil sector is a term commonly used to refer to the refining of crude oil, selling and distribution of natural gas and products derived from crude oil. Such products include liquified petroleum gas (LPG), gasoline or petrol, jet fuel, diesel oil, other fuel oils, asphalt and petroleum coke. It also includes oil refineries, petrochemical plants, petroleum product distribution, retail outlets and natural gas distribution companies. The downstream industry touches consumers through thousands of products such as petrol, diesel, jet fuel, heating oil, asphalt, lubricants, synthetic rubber, plastics, fertilizers, antifreeze, pesticides,pharmaceuticals, natural gas and propane.

The downstream oil industry in Nigeria is another key sector in the country's economy. The country has four oil refineries and there are eight oil companies and 750 independents all active in marketing petroleum products. Cross-border smuggling is an ongoing problem and there are frequent reports of large scale corruption in the distribution and marketing chain. The government through its 100% state-owned national oil company, Nigerian National Petroleum Corporation (NNPC) has had an all encompassing control over the industry through its shareholding in all the companies involved and in the setting of wholesale and retail prices.

3.2 Oil Tanker

An oil tanker, also known as a petroleum tanker, is a ship designed for the bulk transport of oil. There are two basic types of oil tankers: the crude tanker and the product tanker. Crude tankers move large quantities of unrefined crude oil from its point of extraction to refineries. Product tankers, generally much smaller, are designed to move petrochemicals from refineries to points near consuming markets. Oil tankers are often classified by their size as well as their occupation. The size classes range from inland or coastal tankers of a few thousand metric tons of deadweight (DWT) to the mammoth tanker of 550,000 DWT. Tankers move approximately 2,000,000,000 metric tons (2.2046×10^9 short tons) of oil every year. Second only to pipelines in terms of efficiency, the average cost of oil transport by tanker amounts to only twoor three United States cents per 1 US gallon (3.8 L).

Some specialised types of oil tankers have evolved. One of these is the naval replenishment oiler, a tanker which can fuel a moving vessel. Combination ore-bulk-oil carriers and permanently moored floating storage units are two other variations on the standard oil tanker design.

Oil tankers have been involved in a number of damaging and high-profile oil spills. As a result, they are subject to stringent design and operational regulations.

3. 2.1 Pipeline Transport

Pipeline transport is the transportation of goods through a pipe. Dmitri Mendeleev first suggested using a pipe for transporting petroleum in 1863. Most commonly, liquid and gases are sent, but pneumatic tubes that transport solid capsules using compressed air have also been used.

As for gases and liquids, any chemically stable substance can be sent through a pipeline. Therefore, sewage, slurry, water, or even beer pipelines exist, but arguably the most valuable are those transporting fuels, oil, natural gas (gas grid) and biofuels.

3.3 Investment

There are risks associated with investment in Nigeria. These can be grouped into three main categories, political activity and civil unrest, border disputes and government underfunding. There is also the continuing problem of corruption within the system.

3.4 Political Activity and Civil Unrest

The issue at the basis of most civil unrest is the equitable sharing of the country's annual oil revenues among its population and the question of the environmental responsibilities of the oil multinationals. Although all multinationals have been targeted in the disputes, Shell has been the main target. Civil unrest has resulted in over 700 deaths since Obasanjo's take over in 1999 and also resulted in the shut in of terminals and flow stations. The situation is exacerbated by corruption within the industry and the government. Obasanjo has committed his government to resolving the problems and cleaning up the industry and the government in terms of corruption.

3.5 Border Disputes

In the complex boundary delimitations of the Niger Delta area, border disputes are common. Cameroon and Nigeria each claim the Bakassi Peninsula located in the Gulf of Guinea and which is believed to contain significant reserves of oil. In February 1994, Cameroon submitted the dispute to the International Court of Justice (ICJ) for settlement, and Nigeria later followed with its own suit to the ICJ. The ICJ began formal hearings in March 1998 but no decision had been reached by mid 1999.

Nigeria is in dispute over Equatorial Guinea's sole ownership of the Zafiro oilfield in Block B from which Mobil began producing in 1996. Elf holds the concession OML 102 in Nigeria; just 3.5 km north of Equatorial Guinea's Block B. Nigeria and Elf contend that the seismic evidence indicates that Zafiro is part of an oilfield that straddles the international boundary between the two countries. In 1998, Elf announced the Ekanga discovery based on two wells drilled in OML 102. Equatorial Guinea claims that the wells were drilled in their territorial waters in Block B. Nigeria has called for a determination of the boundary and the establishment of a joint field operation. Negotiations have met with little success so far.

3.6 Government Underfunding

A recurring problem in the upstream sector is the inability of the NNPC to meet its funding obligations to the JVs. Under JV terms, the NNPC shares costs with its foreign partners. Since 1993, budgetary constraints on the NNPC have resulted in it being unable to meet its JV commitments leading to cut backs in exploration and production. The government is seeking to diversify funding for the industry and alternative funding schemes have been approved for Shell's EA project and are being considered for Elf's development of the Amenam field.

SELF ASSESSMENT EXERCISE 1

1. What do you understand by the following terms as used in the oil industry? (i)Upstream (ii) Downstream.
2. What are the risks associated with investment in Nigeria?

3.7 World Natural Gas Distribution and Production

As is the case with oil, natural gas is unevenly distributed throughout the world. More than one-third of the world's original gas endowment was in the territory of the former Soviet Union. The second largest gas resource, located in the Middle East, comprised about 22% of the world total. Some 17% of the world's original recoverable gas was located in North America. However, North America has accounted for more than one-half of the world's gas production, and now contains only 11% of the world's remaining gas resources. About 38% of the world's remaining gas is in the former Soviet Union and 25% is located in the Middle East. South America, Europe, Africa, and Asia/Oceania are each projected to contain less than 10% of the world's remaining natural gas.

Africa's natural gas reserves lie largely in the North African countries; Algeria, Egypt, and Libya, and in the Gulf of Guinea with Nigeria alone accounting for 36% of proved African reserves.

Thus, the world distribution of natural gas mirrors that of oil, which might be expected since oil and gas are often generated and reservoired together. However, the Middle East, although containing a very significant amount of gas, does not dominate world gas as it does world oil. The former USSR holds the dominant natural gas resource. Also, it is the world's leading gas producer, but its output is only slightly higher than that of North America. North America produces a large amount of gas from a relatively small reserve. Its reserves/production (R/P) ratio of 12/1 contrasts with the 80/1 R/P ratio of the former USSR.

The R/P ratio is a measure of the rate of production of a proved gas reserve. Associated gas is produced along with oil, which can be efficiently recovered at a maximum R/P ratio of about 10/1. Non-associated gas, which is more volatile than oil, can be produced at faster rates sometimes as fast as an R/P ratio of 5/1. Average regional R/P ratios for intensively and efficiently developed natural gas provinces may range between 7/1 and 10/1. In general, the average R/P ratio of a gas province or a country is indicative of its development maturity, for it will consist of a combination of low R/P ratios in older depleting fields and higher R/P ratios in more newly developed fields. Since, the larger fields are usually found early in the exploration cycle (because of their large size and anomalous geology), they will dominate and, with depletion, tend to decrease the average R/P ratio. Any gas reserves that remain undeveloped or are not produced efficiently help to increase average R/P ratios. An average R/P ratio much above 12/1 usually indicates a gas province or country in which new significant discoveries are being made and/or one in which gas development is not intensive or production is not optimised.

North America, and particularly the United States (with an R/P of 9/1), is an intensively developed and mature gas producing region. Russia, with an R/P of 82/1, contains significantly larger gas reserves than does the United States, but its gas output is only 10% higher. The United Kingdom also is intensively developed, producing gas at an R/P ratio of 9/1. Average European gas production is at an R/P ratio of 24/1, indicating that substantial proved reserves remain. In Asia/Oceania, South America, and Africa gas reserves are underdeveloped, with average R/P ratios ranging from 54/1 to 131/1. The Middle East, with its moderate gas output and enormous gas reserves, has an R/P of 409/1.

3.9 World Natural Gas Consumption and Trade

The global market for natural gas is much smaller than for oil because gas transport is difficult and costly, due to relatively low energy content in relation to volume. Currently, only about 16% of global gas production is internationally traded, with less than 4% of the trade accounted for by LNG. In spite of the high cost of gas transportation and the remote location of some future supply regions, increasing international trade in natural gas is expected.

Global gas reserves are abundant, but of an uneven distribution. The North American market is self sufficient in natural gas, although gas is traded within the region. Canada is expected to remain a net exporter of gas to the United States. Substantial natural gas reserves are located in Europe. The gas trade within the region is extensive, with Norway and the Netherlands the main sources. Europe, however, is and will increasingly become more dependent on gas imported from other regions. Its traditional foreign suppliers, the former Soviet Union (at 20% of demand) and Algeria (at 10%), are expected to increase their shares of the European gas market. Important gas exporters in the Asia-Pacific region are Indonesia, Malaysia, Brunei, and Australia, the gas being shipped as LNG to Japan, Taiwan, and South Korea. The Middle East is another important supply center for natural gas. Abu Dhabi and Qatar deliver significant volumes of LNG to the Asia-Pacific region and future exports could be sent to Europe and South Asia. Gas demand in Africa, South Asia, and China are met by domestic or regional supplies. Some gas is being traded within South America.

The United States consumes about 2.4 tcf more natural gas per year than it produces. Germany imports even more gas than the United States (2.6 tcf per year) and Japan slightly less (2.3 tcf per year). North America is the leading consumer of natural gas, but also is a leading producer. The former USSR region leads the world in gas production, and is second in consumption. Europe ranks third in natural gas consumption, but has to import 4.1 tcf per year. Asia/Oceania also must import natural gas to satisfy demand. The other regions are relatively minor producers and consumers of gas.

Compared to oil, only moderate amounts of natural gas are traded on world markets. The low density of gas makes it more expensive to transport than oil. A section of pipe in oil service can hold 15 times more energy than when used to transport high pressure gas. Thus, gas pipelines must be of larger diameter to a given energy movement. Compression adds to the disparity between the transportation costs of the two fuels. An oil pumping station uses energy to overcome frictional losses, but a gas line requires a large amount of energy to compress the gas before pipeline friction is even encountered.

Pipeline transportation is not always feasible because of the growing geographic distance between gas reserves and markets. Also, since potential political instabilities may affect long pipeline routes, importing countries may wish to diversify supply sources. While natural gas can be piped in a gaseous state, it needs to be condensed (liquified) in order that sufficient energy is packaged to be economically transported by ship. A full liquefied natural gas (LNG) chain consists of a liquefaction plant; low temperature, pressurised, transport ships, and a regasification terminal. World LNG trade is currently about 60 million metric tons per year, some 65% of which is imported by Japan. Other importers include France, Spain, Korea, Belgium, Taiwan, and Italy. Indonesia accounts for 39% of LNG exports, with Algeria in second place with 24%. Other exporters include Malaysia, Brunei, Australia, Abu Dhabi, and Libya. The United States imports and exports about 1 million metric tons of LNG per year. No grassroots LNG project has been commissioned since 1989 due to intense competition with other fuels, notably oil (the world price of which remains low).

Table 4: Current Regional Natural Gas Status (in tcf)

Region	Current Production	Proved Reserves	- R/P Ratio	Current Consumption
North America	25.5	312.7	12/1	24.4
South America	2.1	189.1	90/1	2.7
Europe	9.2	216.3	24/1	13.3
Former USSR	25.7	2057.5	80/1	20.9
Africa	2.6	341.6	131/1	1.6
Middle East	3.9	1594.3	409/1	4.7
Asia/Oceania	6.5	350.6	54/1	7.8
TOTAL WORLD	75.5	5062.1	67/1	75.4

(Source: http//en.wikipedia.org/wiki/file)

Nigeria has a population of over 110 million people and an abundance of natural resources, especially hydrocarbons. It is the 10th largest oil producer in the world, the third largest in Africa and the most prolific oil producer in Sub-Saharan Africa. The Nigerian economy is largely dependent on its oil sector which supplies 95% of its foreign exchange earnings.

The upstream oil industry is Nigeria’s lifeblood and yet it is also central to the ongoing civil unrest in the country, which gained worldwide publicity with the trial and execution of Ken Saro Wiwa, and eight other political activists in 1995. The upstream oil industry is the single most important sector in the economy. According to the 2008 BP Statistical Energy Survey, Nigeria had proved oil reserves of 36.22 billion barrels at the end of 2007 or 2.92% of the world's reserves.

Table 5: Regional Natural Gas Distribution (in tcf)

Region	Undiscovered Resources	Original Gas Endowment	Cumulative Production	Remaining Gas
North America	856.5	2118.3	949.1	1169.2
South America	291.1	523.9	43.7	480.2
Europe	299.9	736.4	220.2	516.2
Former USSR	1840.0	4358.9	461.4	3897.5
Africa	411.4	788.7	35.7	753.0
Middle East	1013.7	2665.7	57.7	2608.0
Asia/Oceania	561.4	998.1	86.1	912.0
TOTALWORLD	5274.0	12190.0	1853.9	10336.1

(Source: http//en.wikipedia.org/wiki/file)

The Nigerian government planned to expand its proven reserves to 40 billion barrels by 2010. Most of this is produced from the prolific Niger Delta. Despite problems associated with ethnic unrest, border disputes and government funding, Nigeria’s wealth of oil makes it most attractive to the major oil-multinationals, most of them are represented in Nigeria, with the major foreign stakeholder being Shell. Nigeria produced an average of 2355.8 thousand barrels of crude oil per day in 2007, 2.92% of the world total and a change of -4.8% compared to 2006.

According to the 2008 BP Statistical Energy Survey, Nigeria had 2007 proved natural gas reserves of 5.29 trillion cubic metres, 2.98% of the world total. Due, mainly, to the lack of a gas infrastructure, 75% of associated gas is flared and 12% re-injected. Nigeria set a target of zero flare by 2010 and is providing incentives for the production and use of gas. The government also plans to raise earnings from natural gas exports to 50% of oil revenues by 2010. It has been reported in the 2008 BP Statistical Energy Survey that Nigeria had 2007 natural gas production of 34.97 billion cubic metres, 1.18% of the world total. However, it should be noted that great controversy, reflecting differing societal values, surrounds the search for and development of gas, as opponents to drilling cite potential environmental damage.

Nigeria's downstream oil industry is also a key sector including four refineries with a nameplate capacity of 438,750 bbl/d. Problems such as fire, sabotage, poor management, lack of turnaround maintenance and corruption have meant that the refineries often operate at 40% of full capacity, if at all. This has resulted in shortages of refined product and the need to increase imports to meet domestic demand. Nigeria has a robust petrochemicals industry based on its substantial refining capacity and natural gas resources. The petrochemical industry is focused around the three centres of Kaduna, Warri and Eleme.

Until 1960, government participation in the oil industry was limited to regulation and administration of fiscal policies. In 1971, Nigeria joined OPEC and in line with OPEC resolutions, the Nigerian National Oil Corporation (NNOC) was established, later becoming NNPC in 1977. This giant parastatal, with all its subsidiary companies, controls and dominates all sectors of the oil industry, both upstream and downstream.

In April 2000, the Nigerian government set up a new committee on oil and gas reform to deal with the deregulation and privatisation of NNPC. Seven subsidiaries of NNPC are due to be sold including the three refineries, the Eleme Petrochemicals Company Ltd, the Nigerian Petroleum Development Company and the partially owned oil marketing firm, Hyson Nigeria Ltd.

The petroleum industry in Nigeria is regulated by the Ministry of Petroleum Resources. The government retains close control over the industry and the activities of the NNPC, whose senior executives are appointed by the ruling government.

SELF ASSESSMENT EXERCISE 2

1. Define the following terms:

(i) Oil tanker (ii) Pipeline transport (iii) Reserve/production ratio.

2. Why is the global market for natural gas much smaller than for oil?

4.0 CONCLUSION

This unit examined the world gas distribution, production, and consumption it also examined the global markets for natural gas. In order to encourage increased domestic drilling, and, thus, future domestic gas production, all the problems associated with investment in gas production must be addressed. However, great controversy, reflecting differing societal values and environmental damage must also be resolved especially with the indigenous populace around the gas / oil fields.

5.0 SUMMARY

In this unit, you have learnt that:

- Natural gas is unevenly distributed throughout the world.
- More than one-third of the world’s original gas endowment was in the territory of the former Soviet Union.
- Africa’s natural gas reserves lie largely in the North African countries; Algeria, Egypt, and Libya, and in the Gulf of Guinea with Nigeria alone accounting for 36% of proved African reserves
- World natural gas consumption is rising faster than that of any other fossil fuel.
- About two-thirds of the increase in gas demand is in the industrial and power generation sectors while the remaining one-third is in heating of buildings and homes.
- North America is the leading consumer and producer of natural gas.
- Moderate amounts of natural gas are traded on world markets
- The low density of gas makes it more expensive to transport than oil.
- The upstream oil sector is a term commonly used to refer to the searching for and the recovery and production of crude oil and natural gas, and the downstream oil sector is a term commonly used to refer to the refining of crude oil, selling and distribution of natural gas and products derived from crude oil.
- There are risks associated with investment in Nigeria and this include political activity and unrest, border disputes and government underfunding which is a recurring problem in upstream sector.

7.0 TUTOR-MARKED ASSIGNMENT

1. Why is the global market for natural gas is much smaller than for oil
2. World natural gas consumption is rising faster than that of any other fossil fuel. Discuss.
3. Discuss the various modes of transporting petroleum products from refinery to the consumers.

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UNIT 2 NIGERIA NATURAL GAS POTENTIAL

CONTENTS

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. For instance, the word ‘gas’ itself has a variety of different uses and meanings. Therefore in this unit, we shall look at the potential of Nigeria gas, the cost of production, the infrastructure that is available for the production of natural gas in Nigeria, the problems associated with investment in natural gas production, the potential market and other problems associated with Nigerian gas production.

2.0 OBJECTIVES

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

discuss the potential of Nigeria gas
explain the cost of production of natural gas
list infrastructure that is available for the production of Natural gas in Nigeria
enumerate the potential market for natural gas
state the problems associated with Nigerian Gas production.

7.0 MAIN CONTENT

3.1 Nigeria Natural Gas: A Transition from Waste to Resources

The decree issued by the Nigerian government to stop the flaring of natural gas in hydrocarbon exploration and production (E&P) activities by 2008 is an effort to realise commercial benefits from the nation's huge gas reserves. Nigeria has more than 250 oil and gas fields, with about 2,600 producing oil wells and a total oil production of about 2 million barrels per day (mb/d). The proven oil reserves are estimated at 27 billion barrels while the proven gas reserves, consisting of about 50% associated and 50% non-associated gas stand at 124 trillion cubic feet (tcf), or about 21 billion barrels of oil equivalent. This is one-third of Africa's total gas reserves. Nigeria is the ninth largest gas producer in the world and a major potential gas supplier. The proved, probable and possible gas reserves are about 300 tcf.

Oil provides annual revenue of $10 billion for Nigeria and accounts for 90% of the nation's total export earnings and 75% of the gross domestic product. In 2000, the Nigerian president declared that "within four years, revenue from gas will not only be substantial but will nearly be equal to that of crude oil." Although the plan is ambitious, if the government pursues it rigorously, it has the opportunity to generate close to $10 billion per year from sales of natural gas produced in the country in the next few years.

In the past, exploration and production efforts have concentrated on oil while the associated gas has been treated as a waste. As at 2002, Nigeria has produced approximately 19 billion barrels of oil since production started in 1960. Total gas production is currently estimated at approximately 1.9 tcf per year, with an average of 850 billion cubic feet (bcf) per year being flared. The amount of gas flared would result in equivalent annual revenue loss of $2.5 billion at an average gas price of $3 per thousand cubic feet (mcf). Based on our own estimation of gas production, the country has flared an amount of gas capable of paying off its national debt, which stands at $31 billion. If the production rate is maintained, Nigeria has the capability to produce gas for the next 70 years based on the production-to-reserves ratio. This is a larger production-to-reserves ratio than for oil.

The natural gas price in Nigeria is currently very low, ranging from $0.20/mcf to $0.65/mcf. Domestic demand for gas is principally from the power sector and the fertilizer, aluminum smelting, steel and cement industries. To realise value for natural gas produced in Nigeria, a substantial export market must be found.

The worldwide proven natural gas reserves are estimated to be about 5,300 tcf, while the world gas demand is 225 bcf per day, giving a production-to-reserves ratio equivalent to 60 years of production. The United States, Western Europe and Japan account for half of the world's gas consumption, but between them, they account for less than one-fifth of the world's natural gas reserves. They rely on imports from gas-producing countries to meet their demand. Gas supply to the consuming countries is mainly in the form of pipelines and, increasingly, liquefied natural gas (LNG).

LNG trade is economically attractive at a minimum gas price range of $2.50 to $3.50 per mcf. The gas price has not been in this range during most of the past 10 years, thus discouraging the LNG market. More important, because of the scarcity of trade, there has not been an internationally and widely accepted price for natural gas, as there has been for oil.

In the last three years, these trends have significantly reversed, as forecasts of natural gas demand have greatly outpaced the supply, and prices have spiked at over $10/mcf. With demand already rising, coupled with depleted gas reserves in the consuming countries, the gas price is likely at least to stabilise at a price range that will make the LNG trade economically attractive for a long time to come. Most probably, natural gas prices will be maintained considerably above this range until LNG becomes a reality in a massive way. This position was recently buttressed by the pronouncement by U.S. Federal Reserve Chairman Alan Greenspan.

Nigeria has been targeted clearly as a major oil producer for the next decade, especially from the offshore blocks, but its potential for gas production has been underestimated thus far. The quota from the Organisation of the Petroleum Exporting Countries (OPEC) for the member countries regulates oil activities. Although OPEC has not set specific quota for gas production from member countries, constraint on oil production limits the amount of associated gas that can be produced daily. This constraint can be overcome if discoveries of non-associated gas are made. Recently, a total of 13 tcf of non-associated gas reserves were discovered in Bosi and Doro deepwater blocks at a depth of less than 4,500 feet.

The OPEC World Energy Models forecast that world oil demand will rise from 76 million barrels per day in 2000 to 103 million barrels per day in 2020. In spite of this large increase, the oil share of energy demand will decline from 41- 38%, while the gas share of world energy demand will rise from 22 - 27%. Some suggest that gas utilisation would be much higher than the conventional estimates, predicting instead that by 2020, gas would account for 45-50% of the worldwide energy demand while oil will be reduced to 25%.

In spite of such differences, there is universal agreement in all forecasts that gas utilisation will increase substantially, causing a decrease in the oil share over the next two decades. This provides a major incentive for Nigeria to produce much more natural gas and export it as LNG to places of ever-increasing demand.

3.2 Nigeria’s Natural Gas Potential

Nigeria’s natural gas reserves are found in relatively simple geologic structures along the country’s coastal Niger Delta and the offshore blocks. Other prospective hydrocarbon-bearing basins have yet to be fully explored, including the Benin basin, Anambra basin, Benue trough, Bida basin and Chad basin.

Most of the proven gas reserves are found as associated gas in the Niger Delta basin, while the majority of the non-associated gas has been discovered in the offshore blocks. The proven gas reserves of Nigeria are 124 tcf, and 90% of hydrocarbon reservoirs in Nigeria contain potential commercial volume gas-caps. Lack of interest in gas exploration in previous years has resulted in commercial reserves of gas being locked in. This situation will improve with increased efforts to drill for gas. If the theory of finding huge gas reserves in deepwater fields holds true for Nigeria, then there are surprises yet to be discovered in the huge deepwater region.

3.3 Accessibility and Infrastructure

Nigeria has often been referred to as a country with large reserves of “stranded” gas. The current infrastructure for the use of gas inside Nigeria includes a transportation network and some gas utilisation projects.

When the producing oil field is located onshore, whether land or swamp, the producing well is tied to a flow station. A flow station serves as the collection centre for many wells, and the facility is used to separate gas from the remaining hydrocarbon fluid. Much of the separated gas is flared at the flow station, little quantity is sent to the gas-gathering system for treatment for domestic or export use. Gas-producing fields are connected directly to processing plants for treatment.

However, if the well is located in shallow waters, it may be tied to a fixed platform where the gas is partially separated from the remaining hydrocarbon fluid. Developed wells in shallow waters have recently been tied to floating production facilities where full treatment occurs for export purposes. Offshore wells are developed with the use of floating production and storage facilities, which enable full treatment and storage of the hydrocarbon for immediate export.

Operators have embarked on the construction of a gas-gathering system that will collect the gas that had previously been flared at the flow stations. The collected gas will be piped to LNG facilities for treatment and export.

Associated gas produced from floating production facilities that are located in the shallow and deepwater areas will be connected via the proposed new offshore gas-gathering system and sent to the nearest LNG facility for treatment and export. The current thinking is either to develop major offshore non-associated gas fields with floating LNG facilities or to pipe the gas to an LNG facility located at the shore. The economics of such big projects is still under review.

Internal gas utilisation includes current and proposed projects. An existing pipeline system supplies treated gas to industries in the southern part of the country. Natural Gas Corporation (NGC), a wholly owned subsidiary of Nigeria National Petroleum Corporation, operates a large share of the transmission network located in the south. Several large gas export projects have been initiated and new ones are planned to ensure that revenues are generated from gas resources and gas flaring is eliminated. The proposed West Africa Gas pipeline project, for example, is expected to supply gas to Nigeria’s neighbours, Benin, Togo and Ghana, for the purpose of power generation.

A recent proposal is to construct a trans-Sahara pipeline that will deliver Nigerian gas to Europe. Capital investment for the pipeline was put at roughly $9 billion with an annual operating cost of $749 million. The project projected a positive internal rate of return at a gas price of $1.50. One of the major challenges for the project, however, is that the proposed pipeline route passes through four countries with difficult logistical and political conditions.

3.4 Potential Market for Nigerian Gas

There are two potential growth markets for Nigerian natural gas: domestic to a lesser degree, and export to a much larger scale. Domestic uses involve power generation, the cement industry, iron and steel plants, petrochemicals, aluminum smelting and distribution for other industrial uses.

3.4.1 Power Sector

The largest single domestic consumer of natural gas is the Power Holding Company of Nigeria (PHCN), accounting for 70% of the gas consumed in the country. The expected growth for power demand for a developing nation like Nigeria is estimated at 8% per year. Power generation and supply in Nigeria is grossly below demand, thereby resulting in underdevelopments in every facet of life. PHCN generates power from two sources: the hydroelectric power generation plant in the Kainji dam and gas-fired electric generation plants located throughout the country. The manufacturing industry is paralysed from erratic supply of energy. Efforts to remedy the situation will propel the country in the path to development and realisation of other resources that are dependent on energy supply.

3.4.2 Cement

Non-gas-fired cement is not competitive with the export market because of its production cost. Nigeria has eight cement plants, only three of which operate above one-quarter of their installed capacity. Production from these three plants meets only 50% of local demand, while the remaining cement is imported. Expected growth in this industry can only happen if local producers can reduce their production costs efficiently and competitively. This can only happen if gas can be supplied at a relatively low cost to other gas plants in the country.

3.4.3 Fertilizer

The Nigerian application of fertilizer averages 13 kilograms per hectare, one of the lowest in Africa. There are opportunities to expand fertilizer utilisation beyond the 800,000 tons per year currently consumed. Fertilizer demand is projected to increase by 6-7% per year over the next 20 years.

3.4.4 Steel

This sector has been dysfunctional for years but has the capability to pick up with change in government policies and privatisation. The two plants owned by the government have the capacity to produce 1.8 million tons of steel per annum but are currently producing only 0.4 million tons. There is a chance for growth in this sector since the demand for steel in the country is currently satisfied by imports and other private-sector mills.

3.4.5 Other Sectors

Other sectors that utilise gas are the small-scale industry and residential consumption of bottled liquid propane gas (LPG). The use of compressed natural gas (CNG) as a substitute for LPG was hurt by the cost of developing the CNG infrastructure. A study that was done in this area indicated that domestic consumers would not be able to afford the cost of purchasing CNG. The anticipated growth case in this small-scale energy demand area is around 7.5% per annum.

The projected growth of the domestic market for gas utilisation depends on a number of factors. They are the enabling environment that allows the public and private sector to invest in the industries, regulations that will encourage oil multinationals to invest in gas-utilisation infrastructure like energy generation, changes in some government monopoly policies and a transparent structure for gas pricing in the country. Figure 2 shows the current and projected utilisation capacity of natural gas for domestic use.

Information derived from Figures 1 and 2 indicate that Nigeria has a capacity to export more than 2 tcf of gas per year for a number of years, in spite of the projected increase in domestic demand.

The export market for Nigerian natural gas started in 1999 after the construction of the Bonny LNG plant, located in Finima, Bonny Island. It was built primarily on reclaimed land. Developed to be one of the world’s major exporters of LNG, the plant site has a capacity to accommodate up to six trains. The base project with two trains was completed in August 1999. An expansion project with one train and associated LPG facilities was finished in November 2002. Development work on the fourth and fifth trains commenced in 1999, with start-up planned for 2005. Nigeria LNG currently provides 7% of the world’s LNG requirements. This figure will rise to 13% when the fourth and fifth trains come on stream, making the country the world’s third largest exporter of LNG.

3.5 Nigeria Gas for the United States Market

For Nigeria to realise an export market price of $3.50, a greater percentage of the volume of gas exported must find its way to the U.S. market, which is already in short supply. We estimate that the U.S. market will be able to absorb 1 tcf/annum of LNG from Nigeria. This will follow the trends of oil export, remembering that the U.S. is also Nigeria's largest market for crude oil.

Projections indicate that the U.S. gas demand between 2000 and 2020 will grow by 60%, and that this growth can be satisfied almost exclusively by imports. The high increase in gas price in the last couple of years confirms that the supply of natural gas in the U. S. is not meeting the demand.

Nigeria started supplying the U.S. with LNG in 2000 with a total supply of 12 billion cubic feet (bcf), compared to Algeria, which supplied 44 bcf. Considering the U.S. future needs of LNG, Nigeria can increase its gas supply to the U.S. for a good price.

SELF ASSESSMENT EXERCISE 1

1. What are the various means of measuring gas?
2. What do you understand by Btu?
3. Where in Nigeria do we have the proven gas reserve?

3.6 Cost of exporting Nigerian Natural Gas

Development of gas infrastructure and gas utilisation projects in Nigeria is very capital intensive. To obtain commercial benefits from natural gas exported from Nigeria, the price of gas in the export market must be greater than the cost of production, liquefaction, transportation and regasification. The most critical of these costs is that of liquefaction, which in most cases represents between 55 and 75% of the total cost.

To appreciate the economics of gas development projects in Nigeria, we will use two classifications based on the source of gas:

non-associated gas produced from offshore fields
associated gas produced from onshore and offshore fields

The gas activation index used is defined as the capital investment required to produce and process 1 mcf/day of gas for export as LNG.

3.7 Cost of Production of Non-Associated Gas in Deep Water Field

The majority of gas produced in Nigeria is associated gas. Commercial reserves of non-associated gas have recently been discovered in the deepwater region. There are two plausible methods for developing the deepwater non-associated gas fields:

construction of floating LNG facilities
gas-to-shore approach

3.8 Cost of Production of Associated Gas from Onshore and Offshore Fields

Associated gas is collected from the flow stations via the gas-gathering systems that are developed in the Niger Delta area. The gas is transported to the LNG plant for export or for distribution via the gas-processing plants for domestic use.

In analysing the project economics of associated gas production, the conditions obtained from the associated gas framework agreement developed by the oil industry for government approval in 1992 is:

All investment necessary to separate oil and gas from the reservoir into useable products is considered part of the oil field development;
Capital investment for facilities to deliver associated gas in useable form at utilisation or designated custody transfer points will be treated for fiscal purposes as part of the capital investment for oil development;
Capital expenditures will be depreciated over five years at 20% per annum for the first four years and 19% in the last year;
The capital allowances will be offset against oil income at a tax rate of 85%; and
The operating expenses for delivery of gas for commercial use and revenues from sales of gas, and products extracted or derived from the gas, will be treated under the fiscal terms for gas producers – that is, at a tax rate of 40% (now 30%).

To calculate the activation index for associated gas up to the point of conversion to LNG, we obtained the capital cost for the upstream activities (notably the cost of providing the gas-gathering system) and the capital cost for liquefaction.

Almost all the values obtained are higher than the highest activation index obtained for most commercial gas projects in the United States. The highest activation index value computed for a U.S. gas project is $2,760/mcf/d. It would appear that gas produced from these projects is not economically attractive for export. For example, Sapele AGG, with an activation index value of $6,692/mscf/d, returns an equilibrium price of $10.34/mscf of gas.

However, the reason the production of associated gas in the Niger Delta may be profitable despite these capital-intensive projects is that a large part of the capital cost is hidden within the project economics of the accompanying oil production as stated in the framework agreement; otherwise, the projects will not be profitable for the operators. A newcomer planning to explore for gas in the onshore fields needs to be aware of this situation. Producing gas that requires a gas-gathering system in the onshore area may be uneconomical, unlike the typical offshore single commercial reserves.

Operators now charge a tariff of $0.30/mcf to supply feed gas to the Bonny LNG plant. This price returns an activation index of $194/mscf/d, which is low, meaning that stranded gas in Nigeria is obviously much cheaper than gas drilled on purpose.

Thus, producing Nigerian onshore natural gas for export may not be as cheap as some now perceive. Much of the capital costs for the gas-gathering projects are embedded in the capital costs associated with oil production.

SELF ASSESSMENT EXERCISE 2

1. Why do you think the production of associated gas in the Niger Delta may be profitable?
2. What are the methods of developing the deep water non-associated gas fields in Nigeria?
3. Define gas activation index as used in this unit.

3.9 Cost of Liquefaction

The cost estimate of constructing an LNG plant that will process 1.35 bcf/d of natural gas either with a floating LNG or onshore LNG plant is put at $2.80 billion. This cost estimate compares favourably with the cost of the recently completed LNG plant in Nigeria. The first phase of the Bonny LNG plant, which cost $2.5 billion, is expected to treat 900 million cubic feet (MMcf) per day of feed gas. The cost estimate gives an average activation index of $2,074/mscf/d and an equilibrium price of

$2.35/mcf for just the liquefaction process. Although some believe the cost of liquefaction could be between $0.80 and $1.00/mcf.

3.10 Cost of Transportation and Regasification

The cost of transporting LNG from a place like Nigeria to the United States and the cost of regasification has been put between $0.80/mcf and $1.05/mcf of natural gas. If the feed gas can be made available at the current tariff price of $0.30/mcf to the liquefaction plant, then the equilibrium price for supplying LNG from Nigeria to the U.S. would be $3.45/mcf.

This price is barely within the perceived acceptable range. However, if we consider the situation of drilling for gas in the deep water, the equilibrium price could be at least $4.25/mcf, which is outside the price range that is currently considered attractive.

3.10.1 Challenges Ahead

There are no adequate clauses either in the Joint Venture Contract Arrangement or the Production Sharing contracts that address the development of major gas projects. Most of these contracts were developed on the assumption that gas is a by-product of oil production. The Nigerian government needs to remove the bottleneck and institutional structure in the gas sector to allow for free-market operation. For the Nigerian government to achieve the no-gas-flaring decree by 2008, both the government and oil companies must be financially committed to the capital-intensive gas-gathering and treatment systems that need to be in place. Also, a ready market must exist to take the entire volume of gas that would be produced from all fields.

The gas price inside Nigeria is very discouraging, and for the oil companies to invest in the no-gas-flaring vision, export markets for the gas must be found that would ensure good return for investment. In addition, transparency, security and a stable political environment are necessary to increase the confidence of foreign investors.

4.0 CONCLUSION

This unit has examined the potential of Nigeria' natural gas and the problems associated with developing the gas sector in Nigeria. Although Nigeria has adequate reserves of associated and non-associated natural gas for development, there is a strong indication that the current efforts and the planned program by the Nigerian government and the oil-producing companies will lead to an increase in gas production that will meet the demand for domestic utilisation with an excess of 2.0 tcf/annum for export in the next two decades.

Because the Nigerian government wants to stop flaring gas, there is an obvious incentive to bring this gas to the export market, likely the U.S., as LNG. This can happen as long as the producers are still willing to sell the gas for $0.30/mcf, which will give an equilibrium price of $3.45/mcf in the U.S. market. However, any additional drilling for gas purpose may give an equilibrium price of $4.25/mcf, which is unattractive by current market perceptions.

5.0 SUMMARY

In this unit, you have learnt that:

- Natural gas is a vital component of the world's supply of energy.
- The decree issued by Nigerian government to stop the flaring of natural gas in hydrocarbon exploration and production activities is an effort to realise commercial benefits from the nation's huge gas reserves.
- In the past exploration and production efforts have concentrated on oil while the associated gas have been treated as a waste.
- The natural gas price in Nigeria is currently very low, and that domestic demand for gas is principally for the power sector fertilizer, aluminium, steel and cements industries.
- Most of the proven gas reserves are found in the Niger Delta basins, while most of the non-associated gas has been discovered in the offshore block.
- There are two potential growth markets for Nigerian natural gas: domestic to a lesser degree, and export to a much larger scale.
- The gas price inside Nigeria is very discouraging, and for the oil companies to invest in the no-gas-flaring vision, export markets for the gas must be found that would ensure good return for investment. In addition, transparency, security and a stable political environment are necessary to increase the confidence of foreign investors.

6.0 TUTOR-MARKED ASSIGNMENT

1. Discuss the different ways of measuring natural gas.
2. What are the potentials of Nigeria Natural Gas?
3. Highlight the infrastructural and accessibility challenges of Nigeria Natural gas.

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UNIT 3 PETROCHEMICALS FROM NATURAL GAS

CONTENTS

1.0 INTRODUCTION

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. Therefore in this unit we shall discuss the different types of petrochemicals that can be obtained from natural gas and crude oil. These include: chemicals based on direct reaction of methane, synthesis gas, chemicals based on synthesis gas, naphtha based chemicals and chemicals from high molecular weight n-paraffins.

2.0 OBJECTIVES

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

- list the chemicals that can be obtained from natural gas
- explain the following methods methanation, oxidation of paraffins, and shift conversion
- state the uses of carbon disulphide.

3.0 MAIN CONTENT

3.1 Chemical Based on Direct Reactions of Methane

A few chemicals are based on the direct reaction of methane with other reagents. These are carbon disulphide, hydrogen cyanide, chloromethanes, and synthesis gas mixture. Currently, a redox fuel cell based on methane is being developed.

3.2 Carbon Disulphide (CS_2)

Methane reacts with sulphur (an active non metal element of group 6A) at high temperatures to produce carbon disulphide. The reaction is endothermic, and activation energy of approximately 160 KJ is required. Activated alumina or clay is used as the catalyst at approximately 675°C and **2** atmospheres. The process starts by vapourising pure sulphur, mixing it with methane, and passing the mixture over the alumina catalyst. The reaction could be represented as:

$$CH_{4\,(g)} + 2S_{2\,(g)} \longrightarrow CS_{2(g)} + 2H_2S_{(g)} \qquad \Delta H°298 = +150\text{ KJ/mol}$$

Hydrogen sulphide, a co-product, is used to recover sulphur by the Claus reaction. A CS_2 yield of 85 to 90% based on methane is anticipated. An alternative route for CS_2 is by the reaction of liquid sulphur with charcoal. However, this method is not used very much.

3.2.1 Uses of Carbon disulphide

Carbon disulphide is primarily used to produce rayon and cellophane (regenerated cellulose). CS_2 is also used to produce carbon tetrachloride using iron powder as a catalyst at 30°C:

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

Sulphur monochloride is an intermediate that is then reacted with carbon disulphide to produce more carbon tetrachloride and sulphur:

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S$$

The net reaction is:

$$CS_2 + 2Cl_2 \longrightarrow CCl_4 + 2S$$

Carbon disulphide is also used to produce xanthate ROC(S) SNa as an ore flotation agent and ammonium thiocyanate as a corrosion inhibitor in ammonia handling systems.

3.3 Hydrogen Cyanide

Hydrogen cyanide (hydrocyanic acid) is a colourless liquid (b.p.25.6°C) that is miscible with water, producing a weakly acidic solution. It is a highly toxic compound, but a very useful chemical intermediate with high reactivity. It is used in the synthesis of acrylonitrile and adiponitrile, which are important monomers for plastic and synthetic fiber production. Hydrogen cyanide is produced via the Andrussaw process using ammonia and methane in presence of air. The reaction is exothermic, and the heat released is used to supplement the required catalyst-bed energy:

$$2CH_4 + 2NH_3 + 3O_2 \longrightarrow 2HCN + 6H_2O$$

A platinum-rhodium alloy is used as a catalyst at 1100°C. Approximately equal amounts of ammonia and methane with 75 vol % air are introduced to the preheated reactor. The catalyst has several layers of wire gauze with a special mesh size (approximately 100 mesh).In Degussa process on the other hand, ammonia reacts with methane in absence of air using platinum, aluminum-ruthenium alloy as a catalyst at approximately 1200°C. The reaction produces hydrogen cyanide and hydrogen, and the yield is over 90%. The reaction is endothermic and requires 251 KJ/mol.

$$CH_4 + NH_3 + 251\ KJ \longrightarrow HCN + 3H_2$$

Hydrogen cyanide may also be produced by the reaction of ammonia and methanol in presence of oxygen:

$$NH_3 + CH_3OH + O_2 \longrightarrow HCN + 3H_2O$$

Hydrogen cyanide is a reactant in the production of acrylonitrile, methyl methacrylates (from acetone), adiponitrile, and sodium cyanide. It is also used to make oxamide, a long-lived fertilizer that releases nitrogen steadily over the vegetation period. Oxamide is produced by the reaction of hydrogen cyanide with water and oxygen using a copper nitrate catalyst at about 70°C and atmospheric pressure.

3.4 Chloromethanes

The successive substitution of methane hydrogens with chlorine produces a mixture of four chloromethanes:

$CH_4 + Cl_2 – CH_3Cl + GCl$
$CH_3Cl + Cl_2 – CH_2Cl_2 + HCl$
$CH_2Cl_2 + Cl_2 – CHCl_3 + HCl$
$CHCl_3 + Cl_2 – CCl_4 + HCl$

Each of these four compounds has many industrial applications that will be dealt with separately.

3.4.1 Production of Chloromethanes

Methane is the most difficult alkane to chlorinate. The reaction is initiated by chlorine free radicals obtained via the application of heat (thermal) or light (*hv*). Thermal chlorination (more widely used industrially) occurs at approximately 350–370°C and atmospheric pressure. A typical product distribution for a CH_4/Cl_2 feed ratio of 1.7 is: mono- (58.7%), di-(29.3%) tri- (9.7%) and tetra- (2.3%) chloromethanes. The highly exothermic chlorination reaction produces approximately 95 KJ/mol of HCl. The first step is the breaking of the Cl–Cl bond (bond energy = + 584.2 KJ), which forms two chlorine free radicals (Cl atoms):

$$Cl_2 \xrightarrow{hv} 2Cl^{\cdot}$$

The Cl atom attacks methane and forms a methyl free radical plus HCl. The methyl radical reacts in a subsequent step with a chlorine molecule, forming methyl chloride and a Cl atom:

$$Cl^{\cdot} + CH_4 \longrightarrow CH_3^{\cdot} + HCl$$

$$CH_3^{\cdot} + Cl_2 \longrightarrow CH_3Cl + Cl^{\cdot}$$

The new Cl atom either attacks another methane molecule to repeat the above reaction, or reacts with a methyl chloride molecule to form a chloromethyl free radical CH_2C_l-and HCl.

$$Cl^{\cdot} + CH_3Cl \longrightarrow CH_2Cl^{\cdot} + HCl$$

The chloromethyl free radical then attacks another chlorine molecule and produces dichloromethane along with a Cl atom:

$$CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl$$

This formation of Cl free radicals continues until all chlorine is consumed. Chloroform and carbon tetrachloride are formed in a similar way by the reaction of $CHCl_2$ and CCl_3 free radicals with chlorine.

Product distribution among the chloromethanes depends primarily on the mole ratio of the reactants. For example, the yield of monochloromethane could be increased to 80% by increasing the CH_4/Cl_2 mole ratio to 10:1 at 450°C. If dichloromethane is desired, the CH_4/Cl_2 ratio is lowered and the monochloromethane recycled. Decreasing the CH_4/Cl_2 ratio generally increases polysubstitution and the chloroform and carbon tetrachloride yield. An alternative way to produce methyl chloride (monochloromethane) is the reaction of methanol with HCl. Methyl chloride could be further chlorinated to give a mixture of chloromethanes (dichloromethane, chloroform, and carbon tetrachloride).

3.4.2 Uses of Chloromethanes

The major use of methyl chloride is to produce silicon polymers. Other uses include the synthesis of tetramethyl lead as a gasoline octane booster, a methylating agent in methyl cellulose production, a solvent, and a refrigerant. Methylene chloride has a wide variety of markets. One major use is as a paint remover. It is also used as a degreasing solvent, a blowing agent for polyurethane foams, and a solvent for cellulose acetate. Chloroform is mainly used to produce chlorodifluoromethane (Fluorocarbon22) by the reaction with hydrogen fluoride:

$$CHCl_3 + 2HF \longrightarrow CHClF_2Cl + 2HCl$$

This compound is used as a refrigerant and as an aerosol propellant. It is also used to synthesise tetrafluoroethylene, which is polymerised to a heat resistant polymer (Teflon):

$$2CHClF_2 \longrightarrow CF_2{=}CF_2 + 2HCl$$

Carbon tetrachloride is used to produce chlorofluorocarbons by the reaction with hydrogen fluoride using an antimony pentachloride ($SbCl_5$) catalyst:

$$CCl_4 + HF \longrightarrow CCl_3F + HCl$$

$$CCl_4 + 2HF \longrightarrow CCl_2F_2 + 2HCl$$

The formed mixture is composed of trichlorofluoromethane (Freon-11) and dichlorodifluoromethane (Freon-12). These compounds are used as aerosols and as refrigerants. Due to the depleting effect of chlorofluorocarbons (CFCs) on the ozone layer, the production of these compounds may be reduced appreciably. Much research is being conducted to find alternatives to CFCs with little or no effect on the ozone layer. Among these are HCFC-123 ($HCCl_2CF_3$) to replace Freon-11 and HCFC-22 ($CHClF_2$) to replace Freon-12 in such uses as air conditioning, refrigeration, aerosol, and foam. These compounds have a much lower ozone depletion value compared to Freon-11, which was assigned a value of 1. Ozone depletion values for HCFC-123 and HCFC-22 relative to Freon-11 equals 0.02 and 0.055, respectively.

3.5 Synthesis Gas (Steam Reforming of Natural Gas)

Synthetic gas may be produced from a variety of feedstock. Natural gas is the preferred feedstock when it is available from gas fields (non associated gas) or from oil wells (associated gas). The first step in the production of synthetic gas is to treat natural gas to remove hydrogen sulphide. The purified gas is then mixed with steam and introduced to the first reactor (primary reformer). The reactor is constructed from vertical stainless steel tubes lined in a refractory furnace. The steam to natural gas ratio varies from 4 – 5 depending on natural gas composition (natural gas may contain ethane and heavier hydrocarbons) and the pressure used. A promoted nickel type catalyst contained in the reactor tubes is used at temperature and pressure ranges of 700–800° C and 30 – 50 atmospheres, respectively. The reforming reaction is equilibrium limited. It is favoured at high temperatures, low pressures, and a high steam to carbon ratio. These conditions minimise methane slip at the reformer outlet and yield an equilibrium mixture that is rich in hydrogen.

The product gas from the primary reformer is a mixture of H_2, CO, CO_2, unreacted CH_4, and steam.

The main stream reforming reactions are:

$$CH_{4\,(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2\,(g)} \qquad H^\circ = +206\ KJ$$

$$H^\circ_{800^\circ C} = +226\ KJ$$

$$CH_{4\,(g)} + 2H_2O_{(g)} \longrightarrow CO_{2\,(g)} + 4H_{2(g)} \qquad H^\circ = +164.8\ KJ$$

For the production of methanol, this mixture could be used directly with no further treatment except the adjustment of $H_2/\ (CO + CO_2)$ ratio to approximately 2:1. For producing hydrogen for ammonia synthesis, however, further treatment steps are needed. First, the required amount of nitrogen for ammonia must be obtained from atmospheric air. This is done by partially oxidizing unreacted methane in the exit gas mixture from the first reactor in another reactor (secondary reforming). The main reaction occurring in the secondary reformer is the partial oxidation of methane with a limited amount of air. The product is a mixture of hydrogen, carbon dioxide, carbon monoxide, plus nitrogen, which does not react under these conditions. The reaction is represented as follows:

$$CH_4 + ½(O_2 + 3.76\ N_2) \longrightarrow CO + 2H_2 + 1.88\ N_2 \quad H° = –32.1\ KJ$$

The reactor temperature can reach over 900°C in the secondary reformer due to the exothermic reaction heat. Typical analysis of the exit gas from the primary and the secondary reformers is shown in Table 1. The second step after secondary reforming is removing carbon monoxide, which poisons the catalyst used for ammonia synthesis. This is done in three further steps, shift conversion, carbon dioxide removal, and methanation of the remaining CO and CO_2.

Table 1: Typical Analysis of Effluent from Primary and Secondary Reformers

Constituent	Primary Reformer	Secondary Reformer
H_2	47	39.0
CO	10.2	12.2
CO_2	6.3	4.2
CH_4	7.0	0.6
H_2O	29.4	27.0
N_2	0.02	17.0

(Source: Chemistry of Petrochemical Processes)

3.6 Shift Conversion

The product gas mixture from the secondary reformer is cooled then subjected to shift conversion. In the shift converter, carbon monoxide is reacted with steam to give carbon dioxide and hydrogen. The reaction is exothermic and independent of pressure:

$$CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)} \quad H° = –41\ KJ$$

The feed to the shift converter contains large amounts of carbon monoxide which should be oxidized. An iron catalyst promoted with chromium oxide is used at a temperature range of 425–500°C to enhance the oxidation. Exit gases from the shift conversion are treated to remove carbon dioxide. This may be done by absorbing carbon dioxide in a physical or chemical absorption solvent or by adsorbing it using a special type of molecular sieves. Carbon dioxide, recovered from the treatment agent as a byproduct, is mainly used with ammonia to produce urea. The product is a pure hydrogen gas containing small amounts of carbon monoxide and carbon dioxide, which are further removed by methanation.

SELF ASSESSMENT EXERCISE 1

1. What are the two constituents of synthetic gas?
2. List the chemicals that are based on the direct reaction of methane
3. List the four chloromethanes that are produced by successive substitution of methane

3.7 Methanation

Catalytic methanation is the reverse of the steam reforming reaction. Hydrogen reacts with carbon monoxide and carbon dioxide, converting them to methane. Methanation reactions are exothermic, and methane yield is favoured at lower temperatures:

$$3H_{2\,(g)} + CO_{(g)} \longrightarrow CH_{4\,(g)} + H_2O_{(g)} \qquad H° = –206\ KJ$$

$$4H_{2\,(g)} + CO_{2\,(g)} \longrightarrow CH_{4\,(g)} + 2H_2O_{(g)} \qquad H° = –164.8\ KJ$$

The forward reactions are also favoured at higher pressures. However, the space velocity becomes high with increased pressures, and contact time becomes shorter, decreasing the yield. The actual process conditions of pressure, temperature, and space velocity are practically a compromise of several factors. Raney nickel is the preferred catalyst. Typical methanation reactor operating conditions are 200–300°C and approximately 10 atmospheres. The product is a gas mixture of hydrogen and nitrogen having an approximate ratio of 3:1 for ammonia production. Figure 1 shows the ICI process for the production of synthesis gas for the manufacture of ammonia.

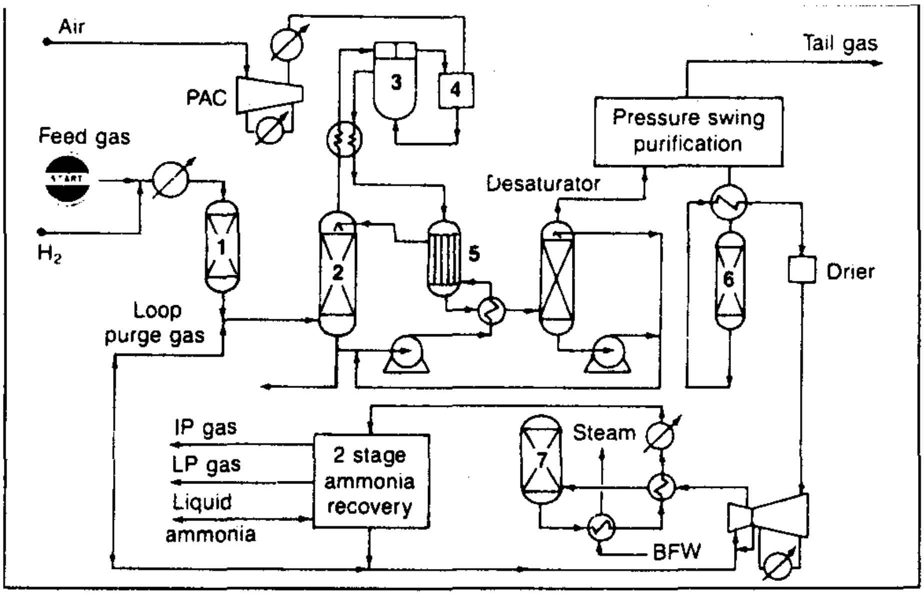

Fig. 1 : The ICI Process for Producing Synthetic Gas and Ammonia; (1) desulphurisation, (2) feed gas saturator, (3) primary reformer, (4) secondary reformer, (5) shift converter, (6) methanator, (7) ammonia reactor.

(Source: Chemistry of Petrochemical Processes)

3.8 Chemicals Based on Synthetic Gas

Many chemicals are produced from synthetic gas. This is a consequence of the high reactivity associated with hydrogen and carbon monoxide gases, the two constituents of synthetic gas.

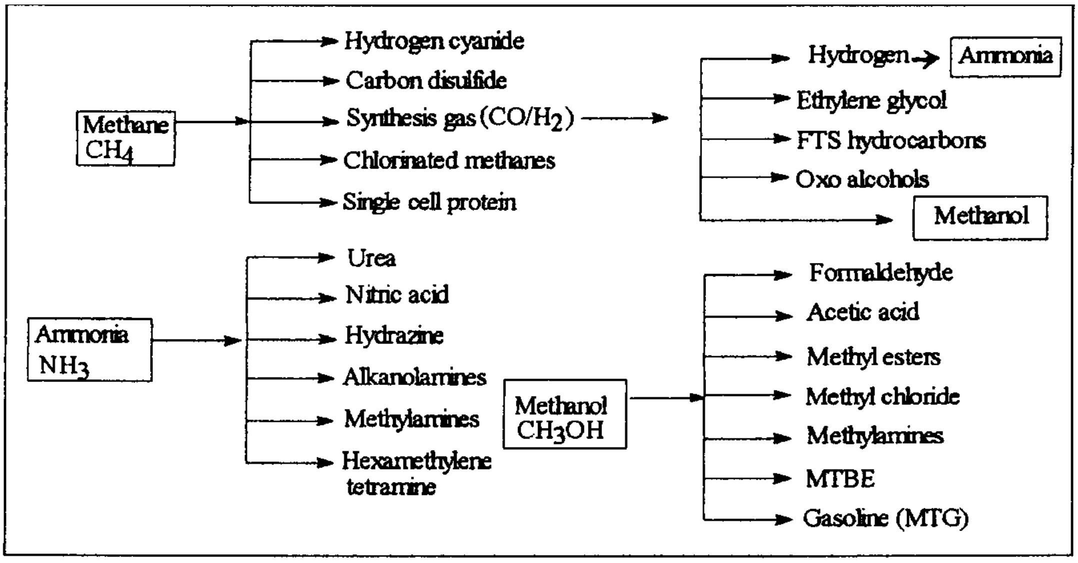

Fig. 2: Important Chemicals Based on Methane, Synthetic Gas, Ammonia, and Methanol

(Source: Chemistry of Petrochemical Processes)

The reactivity of this mixture was demonstrated during World War II, when it was used to produce alternative hydrocarbon fuels using Fischer Tropsch technology. The synthesis gas mixture was produced then by gasifying coal. Synthesis gas is also an important building block for aldehydes from olefins. The catalytic hydroformylation reaction (Oxo reaction) is used with many olefins to produce aldehydes and alcohols of commercial importance. The two major chemicals based on synthesis gas are ammonia and methanol. Each compound is a precursor for many other chemicals. From ammonia, urea, nitric acid, hydrazine, acrylonitrile, methylamines and many other minor chemicals are produced (Fig. 2). Each of these chemicals is also a precursor of more chemicals. Methanol, the second major product from synthesis gas, is a unique compound of high chemical reactivity as well as good fuel properties. It is a building block for many reactive compounds such as formaldehyde, acetic acid, and methylamine. It also offers an alternative way to produce hydrocarbons in the gasoline range (Mobil to Gasoline MTG process). It may prove to be a competitive source for producing light olefins in the future.

3.8.1 Ammonia (NH_3)

This colorless gas has an irritating odour, and is very soluble in water, forming a weakly basic solution. Ammonia could be easily liquefied under pressure (liquid ammonia), and it is an important refrigerant. Anhydrous ammonia is a fertilizer by direct application to the soil. Ammonia is obtained by the reaction of hydrogen and atmospheric nitrogen, the synthetic gas for ammonia. The 1994 U.S. ammonia production was approximately 40 billion pounds (sixth highest volume chemical).

3.8.2 Ammonia Production (Haber Process)

The production of ammonia is of historical interest because it represents the first important application of thermodynamics to an industrial process. Considering the synthesis reaction of ammonia from its elements, the calculated reaction heat (ΔH) and free energy change (ΔG) at room temperature are approximately –46 and –16.5 KJ/mol, respectively. Although the calculated equilibrium constant Kc = 3.6 × 10^8 at room temperature is substantially high, no reaction occurs under these conditions, and the rate is practically zero. The ammonia synthesis reaction could be represented as follows:

$$N_2\ (_g) + 3H_{2\ (g)} \longrightarrow 2NH_{3\ (g)} \qquad \Delta H° = –46.1\ KJ/mol$$

Increasing the temperature increases the reaction rate, but decreases the equilibrium (Kc at 500°C = 0.08). According to Le Chatlier’s principle, the equilibrium is favoured at high pressures and at lower temperatures. Much of Haber's research was to find a catalyst that favoured the formation of ammonia at a reasonable rate at lower temperatures. Iron oxide promoted with other oxides such as potassium and aluminum oxides is currently used to produce ammonia in good yield at relatively low temperatures.

In a commercial process, a mixture of hydrogen and nitrogen (exit gas from the methanator) in a ratio of 3:1 is compressed to the desired pressure (150 – 1,000 atmospheres). The compressed mixture is then pre-heated by heat exchange with the product stream before entering the ammonia reactor. The reaction occurs over the catalyst bed at about 450°C. The exit gas containing ammonia is passed through a cooling chamber where ammonia is condensed to a liquid, while unreacted hydrogen and nitrogen are recycled (Fig. 2). Usually, a conversion of approximately 15% per pass is obtained under these conditions.

3.8.3 Uses of Ammonia

The major end use of ammonia is the fertilizer field for the production of urea, ammonium nitrate and ammonium phosphate, and sulphate. Anhydrous ammonia could be directly applied to the soil as a fertilizer. Urea is gaining wide acceptance as a slow-acting fertilizer. Ammonia is the precursor for many other chemicals such as nitric acid, hydrazine, acrylonitrile, and hexamethylenediamine. Ammonia, having three hydrogen atoms per molecule, may be viewed as an energy source. It has been proposed that anhydrous liquid ammonia may be used as a clean fuel for the automotive industry. Compared with hydrogen, anhydrous ammonia is more manageable. It is stored in iron or steel containers and could be transported commercially via pipeline, railroad, tanker, cars, and highway tanker trucks. The oxidation reaction could be represented as:

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O \quad \Delta H = -316.9 \text{ KJ/mol}$$

Only nitrogen and water are produced. However, many factors must be considered such as the coproduction of nitrogen oxides, the economics related to retrofitting of auto engines, etc. The following describes the important chemicals based on ammonia.

3.8.4 Urea

The highest fixed nitrogen-containing fertilizer 46.7 wt %, urea is a white solid that is soluble in water and alcohol. It is usually sold in the form of crystals, prills, flakes, or granules. Urea is an active compound that reacts with many reagents. It forms adducts and clathrates with many substances such as phenol and salicylic acid. By reacting with formaldehyde, it produces an important commercial polymer (urea formaldehyde resins) that is used as glue for particle board and plywood.

3.8.5 Production of Urea

The technical production of urea is based on the reaction of ammonia with carbon dioxide. The reaction occurs in two steps: ammonium carbamate is formed first, followed by a decomposition step of the carbamate to urea and water. The first reaction is exothermic, and the equilibrium is favoured at lower temperatures and higher pressures. Higher operating pressures are also desirable for the separation absorption step that results in a higher carbamate solution concentration. A higher ammonia ratio than stoichiometric is used to compensate for the ammonia that dissolves in the melt. The reactor temperature ranges between 170–220°C at a pressure of about 200 atmospheres.

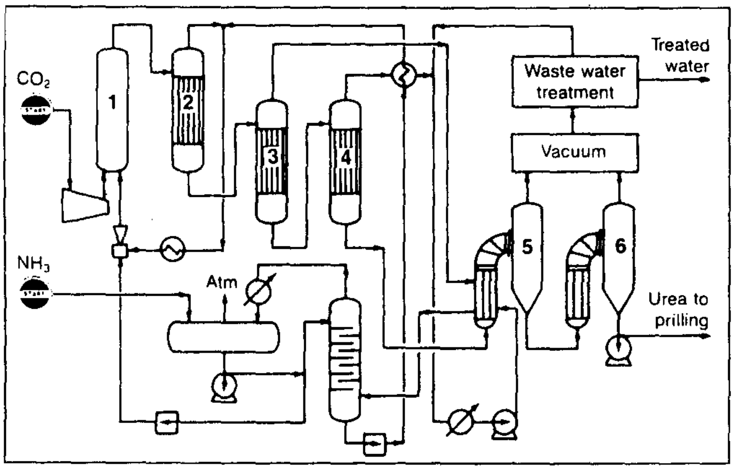

Fig. 3 : The Snamprogetti Process for Producing Urea; (1) Reactor, (2,3,4) Carbonate Decomposer, (5,6) Crystallising and Prilling
(Source: Chemistry of Petrochemical Processes)

The second reaction represents the decomposition of the carbamate. The reaction conditions are 200°C and 30 atmospheres. Decomposition in presence of excess ammonia limits corrosion problems and inhibits the decomposition of the carbamate to ammonia and carbon dioxide.

The urea solution leaving the carbamate decomposer is expanded by heating at low pressures and ammonia recycled. The resultant solution is further concentrated to a melt, which is then prilled by passing it through special sprays in an air stream. Figure 3 shows the Snamprogetti process for urea production.

3.8.6 Uses of Urea

The major use of urea is the fertilizer field, which accounts for approximately 80% of its production (about 16.2 billion pounds were produced during 1994 in U.S.). About 10% of urea is used for the production of adhesives and plastics (urea formaldehyde and melamine formaldehyde resins). Animal feed accounts for about 5% of the urea produced.

3.9 Methyl alcohol (CH_3OH)

Methyl alcohol (methanol) is the first member of the aliphatic alcohol family. It ranks among the top 20 organic chemicals consumed in the U.S. The current world demand for methanol is approximately 25.5 million tons/year (1998) and is expected to reach 30 million tons by the year 2002. The 1994 U.S. production was 10.8 billion pounds. Methanol was originally produced by the destructive distillation of wood (wood alcohol) for charcoal production. Currently, it is mainly produced from synthetic gas. As a chemical compound, methanol is highly polar, and hydrogen bonding is evidenced by its relatively high boiling temperature (65°C), its high heat of vaporization, and its low volatility. Due to the high oxygen content of methanol (50% wt), it is being considered as a gasoline blending compound to reduce carbon monoxide and hydrocarbon emissions in automobile exhaust gases. It was also tested for blending with gasoline due to its high octane number.

During the late seventies and early eighties, many experiments tested the possible use of pure (straight) methanol as an alternative fuel for gasoline cars. Several problems were encountered, however, in its use as a fuel, such as the cold engine startability due to its high heat of vapourisation (heat of vapourisation is 3.7 times that for gasoline), its lower heating value, which is approximately half that of gasoline, and its corrosive properties. The subject has been reviewed by Keller. However, methanol is a potential fuel for gas turbines because it burns smoothly and has exceptionally low nitrogen oxide emission levels. Due to the high reactivity of methanol, many chemicals could be derived from it. For example, it could be oxidised to formaldehyde, an important chemical building block, carbonylated to acetic acid, and dehydrated and polymerised to hydrocarbons in the gasoline range (MTG process).

Methanol reacts almost quantitatively with isobutene and isoamylenes, producing methylt-butylether (MTBE) and tertiary amylmethylether (TAME), respectively. Both are important gasoline additives for raising the octane number and reducing carbon monoxide and hydrocarbon exhaust emissions. Additionally, much of the current work is centered on the use of shape-selective catalysts to convert to light olefins as a possible future source of ethylene and propylene.

3.9.1 Production of Methanol

Methanol is produced by the catalytic reaction of carbon monoxide and hydrogen (synthesis gas). Because the ratio of $CO:H_2$ in synthesis gas from natural gas is approximately 1:3, and the stoichiometric ratio required for methanol synthesis is 1:2, carbon dioxide is added to reduce the surplus hydrogen. An energy-efficient alternative to adjusting the $CO:H_2$ ratio is to combine the steam reforming process with auto thermal reforming (combined reforming) so that the amount of natural gas fed is that required to produce a synthesis gas with a stoichiometric ratio of approximately 1:2.05. Figure 4 is a combined reforming diagram. If an auto thermal reforming step is added, pure oxygen should be used. (This is a major difference between secondary reforming in case of ammonia production, where air is used to supply the needed nitrogen).

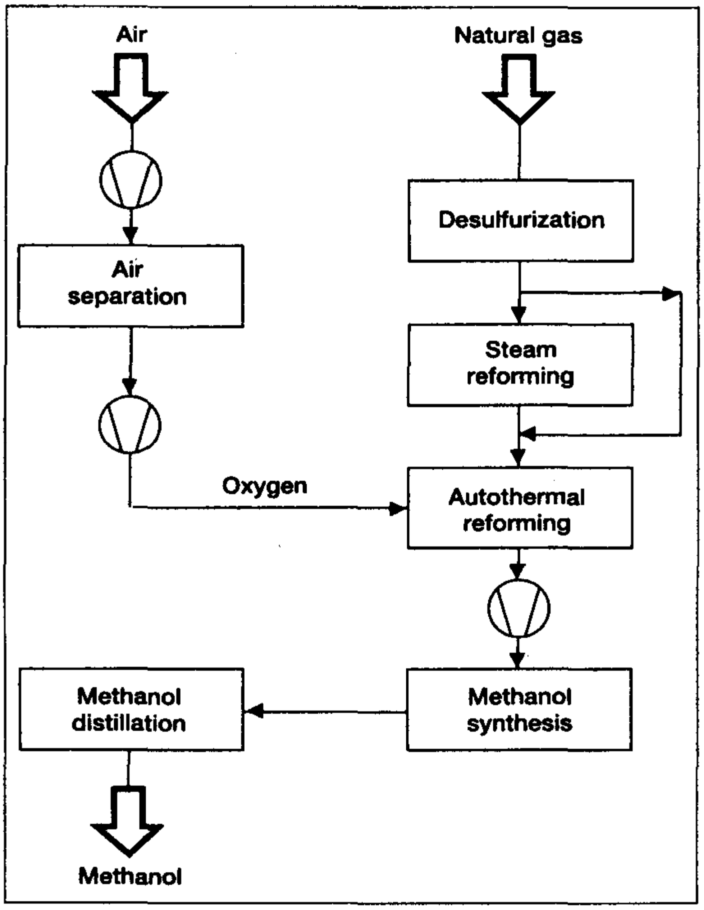

Fig. 4: A Block Flow Diagram Showing the Combined Reforming for Methanol Synthesis

(Source: Chemistry of Petrochemical Processes)

An added advantage of combined reforming is the decrease in NO emission. However, a capital cost increase (for air separation unit) of roughly 15 % is anticipated when using combined reforming in comparison to plants using a single train steam reformer. The process scheme is viable and is commercially proven. The following reactions are representative for methanol synthesis.

$$CO_{(g)} + 2H_{2\,(g)} \longrightarrow CH_3OH_{(1)} \qquad \Delta H° = -128 \text{ KJ/mol}$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

Old processes use a zinc-chromium oxide catalyst at a high-pressure range of approximately 270–420 atmospheres for methanol production. A low-pressure process has been developed by ICI operating at about 50 atm (700 psi) using a new active copper-based catalyst at 240°C. The synthesis reaction occurs over a bed of heterogeneous catalyst arranged in either sequential adiabatic beds or placed within heat transfer tubes. The reaction is limited by equilibrium, and methanol concentration at the converter's exit rarely exceeds 7%. The converter effluent is cooled to 40°C to condense the product methanol, and the unreacted gases are recycled. Crude methanol from the separator contains water and low levels of by-products, which are removed using a two-column distillation system. Figure 5 shows the ICI methanol synthesis process. Methanol synthesis over the heterogeneous catalyst is thought to occur by a successive hydrogenation of chemisorbed carbon monoxide. Other mechanisms have been also proposed.

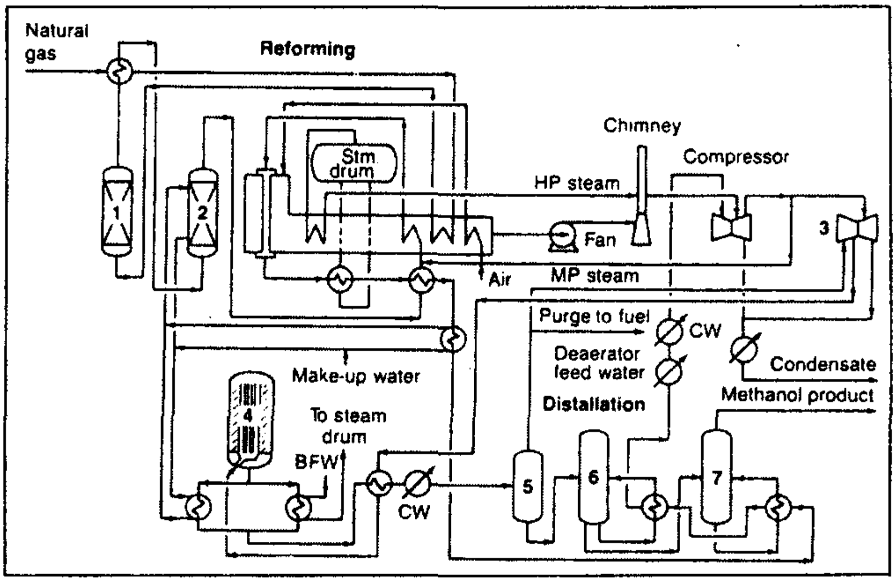

Fig. 5 :The ICI Low – Pressure Process for Producing Methanol; (1) desulphurisation, (2) saturator (for producing steam), (3) synthesis loop circulator, (4) reactor, (5) heat exchanger and separator, (6) column for light ends recovery, (7) column for water

(*Source:* Chemistry of Petrochemical Processes)

3.9.2 Uses of Methanol

Methanol has many important uses as a chemical, a fuel, and a building block. Approximately 50% of methanol production is oxidised to formaldehyde. As a methylating agent, it is used with many organic acids to produce the methyl esters such as methyl acrylate, methylmethacrylate, methyl acetate, and methyl terephthalate. Methanol is also used to produce dimethyl carbonate and methyl-t-butylether, an important gasoline additive. It is also used to produce synthetic gasoline using a shape selective catalyst (MTG process). Olefins from methanol may be a future route for ethylene and propylene in competition with steam cracking of hydrocarbons. The use of methanol in fuel cells is being investigated. Fuel cells are theoretically capable of converting the free energy of oxidation of a fuel into electrical work. In one type of fuel cells, the cathode is made of vanadium which catalyses the reduction of oxygen, while the anode is iron (III) which oxidises methane to CO_2 and iron (II) is formed in aqueous H_2SO_4. The benefits of low emission may be offset by the high cost. The following describes the major chemicals based on methanol.

3.10 Naphtha-based Chemicals

Light naphtha containing hydrocarbons in the C5-C7 range is the preferred feedstock for producing acetic acid by oxidation. Similar to the catalytic oxidation of n-butane, the oxidation of light naphtha is performed at approximately the same temperature and pressure ranges (170–200°C and ≈50 atmospheres) in the presence of manganese acetate catalyst. The yield of acetic acid is approximately 40% wt.

$$\text{Light naphtha} + O_2 \longrightarrow CH_3COOH + \text{by-products} + H_2O$$

The product mixture contains essentially oxygenated compounds (acids, alcohols, esters, aldehydes, ketones, etc.). As many as 13 distillation columns are used to separate the complex mixture. The number of products could be reduced by recycling most of them to extinction. Manganese naphthenate may be used as an oxidation catalyst. Rouchaud and Lutete have made an in-depth study of the liquid phase oxidation of n-hexane using manganese naphthenate. A yield of 83% of C1-C5 acids relative to n-hexane was reported. The highest yield of these acids was for acetic acid followed by formic acid. The lowest yield was observed for pentanoic acid. In Europe naphtha is the preferred feedstock for the production of synthesis gas, which is used to synthesise methanol and ammonia. Another important role for naphtha is its use as a feedstock for steam cracking units for light olefins production. Heavy naphtha, on the other hand, is a major feedstock for catalytic reforming. The product reformates containing a high percentage of C6-C8 aromatic hydrocarbons is used to make gasoline. Reformates are also extracted to separate the aromatics as intermediates for petrochemicals.

3.10.1 Chemicals from High Molecular Weight n-Paraffins

High molecular weight n-paraffins are obtained from different petroleum fractions through physical separation processes. Those in the range of C8-C14 are usually recovered from kerosines having a high ratio of these compounds. Vapour phase adsorption using molecular sieve 5A is used to achieve the separation. The n-paraffins are then desorbed by the action of ammonia. Continuous operation is possible by using two adsorption sieve columns, one bed on stream while the other bed is being desorbed. n- Paraffins could also be separated by forming adduct with urea. For a paraffinic hydrocarbon to form an adduct under ambient temperature and atmospheric pressure, the compound must contain a long unbranched chain of at least six carbon atoms. Ease of adduct formation and adduct stability increases with increase of chain length. As with shorter-chain n-paraffins, the longer chain compounds are not highly reactive. However, they may be oxidised, chlorinated, dehydrogenated, sulphonated and fermented under special conditions. The C9-C17 paraffins are used to produce olefins or monochlorinated paraffins for the production of detergents. The 1996 capacity for the U.S., Europe, and Japan was 3.0 billion pounds.

3.10.2 Oxidation of Paraffins (Fatty Acids and Fatty Alcohols)

The catalytic oxidation of long-chain paraffins (Cl8 – 30) over manganese salts produces a mixture of fatty acids with different chain lengths. Temperature and pressure ranges of 105–120°C and 15–60 atmospheres are used. About 60% wt yield of fatty acids in the range of Cl2-Cl4 is obtained. These acids are used for making soaps. The main source of fatty acids for soap manufacture, however, is the hydrolysis of fats and oils (a non petroleum source). Oxidation of paraffins to fatty acids may be illustrated as:

$$RCH_2(CH_2)nCH_2CH_2R \; ^{+} \; {}^{5}/_{4}O_2 \longrightarrow R(CH_2)_nCOOH + RCH_2COOH + H_2O$$

Oxidation of Cl2 – Cl4 n-paraffins using boron trioxide catalysts was extensively studied for the production of fatty alcohols. Typical reaction conditions are 120–130°C at atmospheric pressure. ter-butyl hydroperoxide (0.5%) was used to initiate the reaction. The yield of the alcohols was 76.2% wt at 30.5% conversion. Fatty acids (8.9% wt) were also obtained. Product alcohols were essentially secondary with the same number of carbons and the same structure½ per molecule as the parent paraffin hydrocarbon. This shows that no cracking has occurred under the conditions used. The oxidation reaction could be represented as:

$$RCH_2CH_2\,R \;+\; \frac{1}{2}O_2 \longrightarrow R\text{-}CH_2CHOH\acute{R}$$

SELF ASSESSMENT EXERCISE 2

1. What are the two chemicals that use synthetic gas as building blocks?
2. What is the effect of increasing temperature in Haber process?
3. List the uses of ammonia and methanol

4.0 CONCLUSION

This unit has been able to show that natural gas and crude oil are the basic raw materials for the manufacture of petrochemicals. In addition, it has also shown that secondary raw materials or intermediates are obtained from light hydrocarbon compounds such as methane and ethane, or from heavier hydrocarbon mixtures such as naphtha or gas oil. Furthermore, we have come to learn that only few chemicals can be produced directly from methane under relatively severe conditions while many other chemicals can be produced from methane via a more reactive synthesis gas mixture.

5.0 SUMMARY

In this unit, you have learnt that:

Carbon disulphide, hydrogen cyanide, chloromethane, and synthetic gas mixture are produced by direct reaction of methane

Carbon disulphide is used to produce rayon, cellophane and carbon tetrachloride

Hydrogen cyanide is used in the synthesis of acrylonitrile and adiponitrile, which are important monomers for plastic and synthetic fibre production.

Successive substitution of methane with chlorine produces a mixture of four chloromethanes namely: monochloromethane, dichloromethane, trichloromethane and tetrachloromethane

The major use of chloromethane is for the production of silicon polymer, other uses include the synthesis of tetramethyl lead, as a methylating agent in methyl cellulose production, as a solvent and refrigerant.

Synthesis gas may be produced from variety of feedstock, however, natural gas is the preferred feedstock when it is available.

Many chemicals are produced from synthesis gas and these include: ammonia, urea, methyl alcohol (methanol).

Hydrocarbons in the C5 – C7 (light naphtha) are the preferred feedstock for producing acetic acid. While high molecular weight n-paraffins are obtained from different petroleum fractions.

6.0 TUTOR-MARKED ASSIGNMENT

1. List and discuss two of the chemicals produced by the direct reaction of methane
2. What are the uses of Carbon disulphide and hydrogen cyanide?
3. Why is methane the most difficult to chlorinate
4. Synthetic gas may be produced from a variety of feedstock, however, natural gas is the preferred feedstock when it is available. Discuss.
5. Methanol has many important uses as a chemical, list them.

7.0 REFERENCES/FURTHER READING

http//www.wikipedia.org

Matar, S. & Hatch, L. F. (1994). *Chemistry of Petrochemical Processes*, Second Edition. Houston: Gulf Publishing Company.