NATIONAL OPEN UNIVERSITY OF NIGERIA

CHM 306

Petroleum Chemistry

Module 3

CHM 306 Petroleum Chemistry Module 3

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Module 3 Distribution of Petroleum and Natural Resources

Unit 1 Distribution of Natural Gases

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

At 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 on-going 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 two or 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. 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

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.

6.0 Self-Assessment Exercise

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

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

At 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.

3.0 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, aluminium 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. 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

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 Self-Assessment Exercise

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

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

At 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:

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

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:

- $CH_4 + Cl_2 – CH_3Cl + GCl$
- $CH_3Cl + Cl_2 – CH_2\ Cl_2 + HCl$
- $CH_2Cl_2 + Cl_2 – CHCl_3 + HCl$
- $CHCl_3 + Cl_2 – CCl_4 + HCl$

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:

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

$$\Delta H°_{800°C} = +226\ KJ$$

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

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:

$$CH_4 + \tfrac{1}{2}(O_2 + 3.76\ N_2) \longrightarrow CO + 2H_2 + 1.88\ N_2 \quad \Delta H° = -32.1\ KJ$$

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:

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

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. 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:

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

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

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.

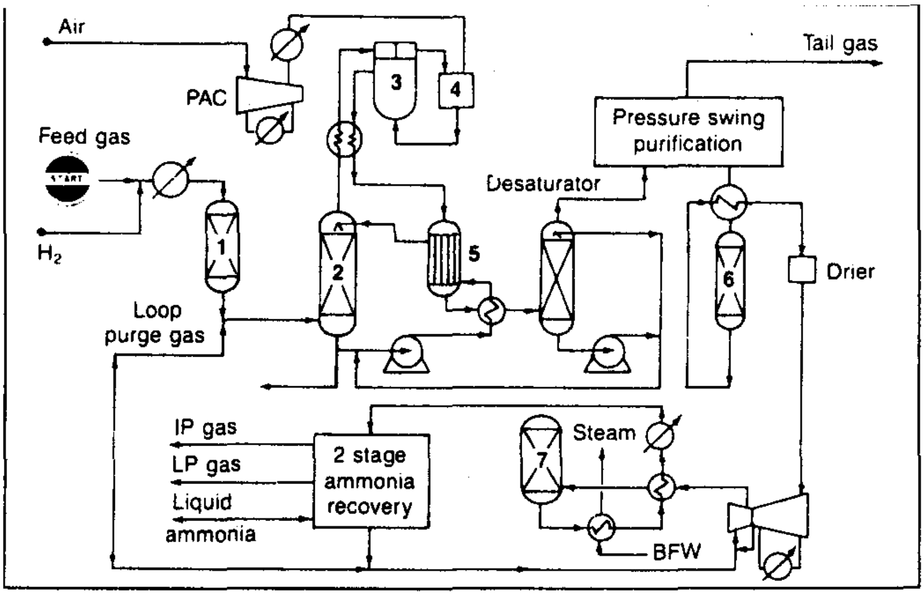

Fig. 1: The ICI Process for Producing Synthetic Gas and Ammonia; (1) desulphurisation, (2) feed gas saturator, (3) primary reformer, (4) secondary reformer, (5) shift converter, (6) methanator, (7) ammonia reactor.

(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.

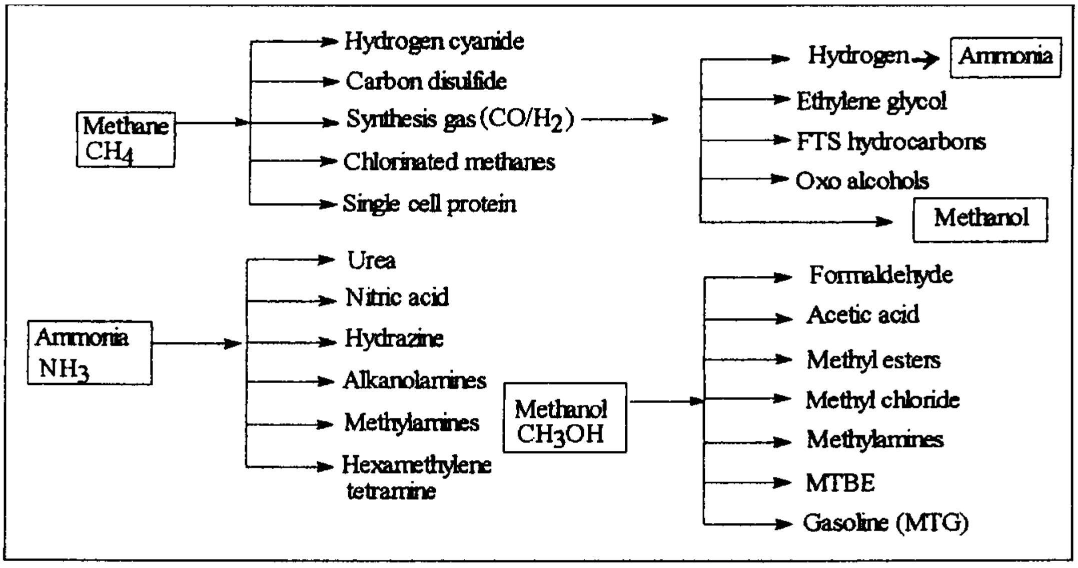

Fig. 2: Important Chemicals Based on Methane, Synthetic Gas, Ammonia, and Methanol

(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 (NH3)

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:

- $N_{2\,(g)} + 3H_{2\,(g)} \longrightarrow 2NH_{3\,(g)}$ $\Delta H° = -46.1$ 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:

- $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$ $\Delta H = -316.9$ 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.

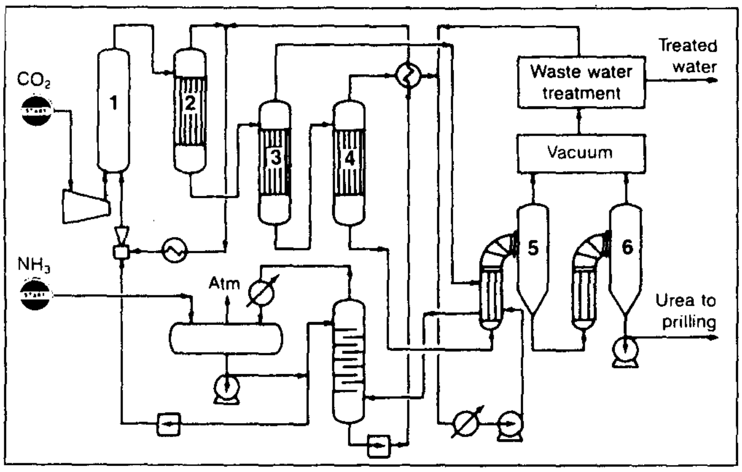

Fig. 3: The Snamprogetti Process for Producing Urea; (1) Reactor, (2,3,4) Carbonate Decomposer, (5,6) Crystallising and Prilling

(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).

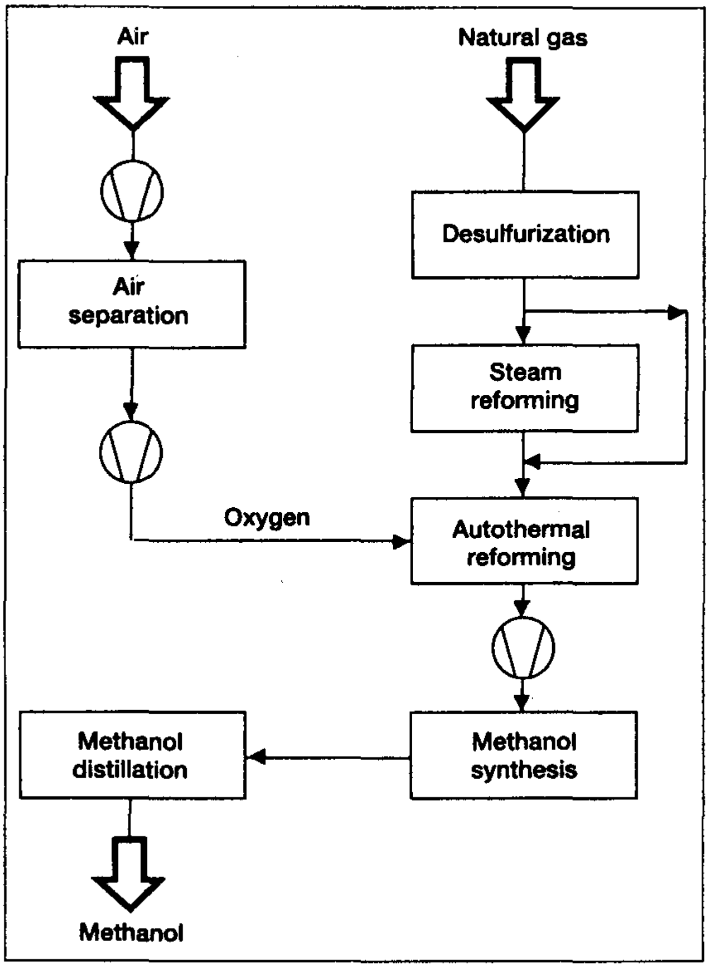

Fig. 4: A Block Flow Diagram Showing the Combined Reforming for

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.

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

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

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.

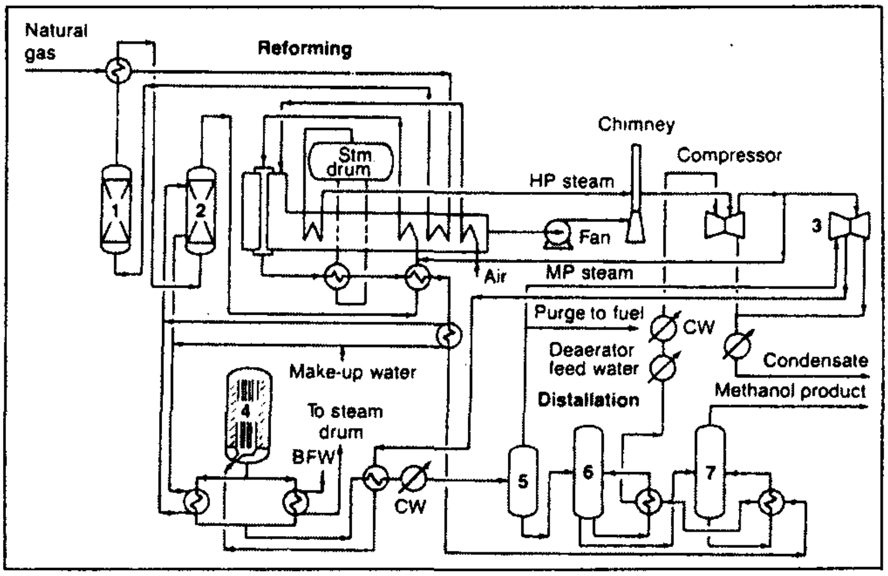

Fig. 5: The ICI Low – Pressure Process for Producing Methanol; (1) desulphurisation, (2) saturator (for producing steam), (3) synthesis loop circulator, (4) reactor, (5) heat exchanger and separator, (6) column for light ends recovery, (7) column for water.

(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:

$$RCH_2(CH_2)nCH_2CH_2R + {}^5/_4O_2 \longrightarrow R(CH_2)_nCOOH + RCH_2COOH + H_2O$$

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:

$$RCH_2CH_2R' + {}^1/_2O_2 \longrightarrow R\text{-}CH_2CHOHR'$$

Self-Assessment Exercise

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 Self-Assessment Exercise

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.