ChemClass Journal, 2005, Volume 2, (25-31)

Development of petrochemicals from natural gas (methane)

N.S. Maina
Department of Chemical Engineering, Ahmadu Bello University, Zaria. 810261. E-mail: nsmaina@yahoo.com

ABSTRACT

Natural gas (methane) is a mixture of hydrocarbon gases along with some impurities that are the result of decomposed organic matter. Due to the variety of its constituents, it finds wide application either as an energy source or as feedstock to chemical and petrochemical industries. Methane is the major constituent of natural gas (95 to 98 %). As a feedstock it is first of all converted to synthesis gas ($CO + H_2$) and then used to manufacture a gamut of intermediate chemicals and finished products such as ammonia, oxoalcohols, chloromethane, methanol, fertilizers, etc. However, ethane is the most desirable feedstock for ethylene production when minimum amount of by-product is desired. Nigeria is endowed with abundant natural gas resources. The country's reserves of natural gas are estimated at 170 trillion cubic feet (TCF). Abundant natural resources are required for economic development, which is a prospect. This paper discusses feasible gas based industries that can emanate from the petroleum industries or oil fields that enhance utilization of natural gas as raw material for the industrial development of the country. This paper also encourages the government to set up industries that could produce intermediate and finished products rather than exporting more liquefied natural gas (LNG) to the developed nations.

INTRODUCTION

A petrochemical is any chemical compound obtained from petroleum or natural gas or derived from petroleum or natural gas hydrocarbons and utilized in chemical markets [1,2]. The definition has been broadened to include the whole range of aliphatic, aromatic, and naphthenic organic chemicals, as well as carbon black and such inorganic materials as sulphur and ammonia [2]. In many instances, a specific chemical included among the petrochemicals may also be obtained from other sources, such as coal, coke, or vegetable products.

Petrochemical products include such items as plastics, soaps and detergents, solvents, drugs, fertilizers, pesticides, explosives, synthetic fibers and rubbers, paints, epoxy resins, and flooring and insulating materials. Petrochemicals are found in products as diverse as aspirin, luggage, boats, automobiles, aircraft, polyester clothes, and recording discs and tapes.

Natural gas and crude oil are referred to collectively as petroleum. Crude oil is merely the heavier constituents that naturally occur in liquid form; while natural gas refers to the lighter constituents of petroleum that naturally occur in gaseous form on its own as free gas, or in association with crude oil [1, 3, 4, 5].

Natural gas has been used commercially as a fuel for 180 years in the America and for centuries in China. The production, processing, and distribution of natural gas have become an important segment of any economy and a major factor in the world markets.

Since its discovery in the United States, reported to be at Fredonia, New York, in 1821, [3] natural gas has been used as fuel in areas immediately surrounding the gas fields. However, as late as the 1930s produced natural gas was flared and blown to the air in large volumes. When gas accompanied crude oil, the gas had to find a market or be flared and, in the absence of effective conservation practices in earlier years, oil-well gas was often flared in huge quantities. The modern natural gas industry began immediately following World War II when a number of long-distance pipelines were constructed to serve markets in the populated areas.

Natural gas processing plants are usually designed to remove certain valuable products over and above those needed to make the gas marketable, that is, natural gasoline, butane, propane, ethane, and even methane in some instances. Plants may also be designed to recover elemental sulphur from hydrogen sulphide gas removal from wellhead gas.

Nigeria is blessed with large reserves of natural gas. The country's reserves of the gas are estimated at 170 trillion cubic feet (TCF) [6]. The natural gas business is growing and changing; creating opportunities and challenges for sellers, buyers, ship owners and traders. Nigeria needs to develop her downstream industries by setting up more industries that could utilize part of the abundant gas resources, such as in petrochemicals and fertilizers, to mention a

few; instead of only exporting the gas as LNG to developed countries. This in the long run will create job opportunities for her citizens.

CHARACTERISTICS OF NATURAL GAS

Natural gas is a mixture of hydrocarbon gases along with some impurities that are the result of decomposed organic matter. The impurities found also include water and heavier hydrocarbons. When raw natural gas is withdrawn from the underground reservoirs to supply energy demands, these impurities are considered objectionable and are usually removed by various processing schemes. The hydrocarbon gases normally found in natural gas are methane, ethane, propane, butanes, pentanes, and small amounts of hexanes, heptanes, octanes, and the heavier gases. Usually the propane and heavier fractions are removed for additional processing because of their high market value as gasoline-blending stock and chemical plant raw feedstock. What usually reaches the transmission line for sale as natural gas is mostly mixture of methane and ethane with some small percentage of propane. Methane is usually the largest percentage (95 to 98 percent). [1, 2, 3, 7]

COMPOSITION OF NATURAL GAS

Natural gas has been defined as a mixture of hydrocarbon gases and impurities. There is no one composition or mixture that can be referred to as natural gas. Each gas stream produced has its own composition. Even two gas wells from the same reservoir may have different compositions. Examples of some typical natural gas streams are provided in Table 1 to show the range of composition that is naturally produced. [2, 3, 7].

Well stream no. 1 is typical of an associated gas; that is, gas produced with crude oil. Well streams no. 2 and no. 3 are typical low-pressure and high-pressure gases of the non-associated type. Not only is there a wide variety of natural gas compositions, but each gas stream produced from natural gas reservoir can change composition as the reservoir is depleted.

Natural gas is normally thought of as being a mixture of straight-chain or paraffin hydrocarbon gases. We have, however, occasionally found cyclic and aromatic hydrocarbon gases (cyclic compounds) in the mixture.

PHYSICAL PROPERTIES OF NATURAL GAS

The overall physical properties of a natural gas are indicators of the behaviour of the gas under various processing conditions, and it is therefore important to be able to establish these physical properties. In order to do this, the analysis or composition of gas must be determined first. Once the composition is known, the various physical properties can be determined by using the physical properties of each pure component in the mixture. Physical properties that are most useful in natural gas processing are molecular weight, freezing point, boiling point, density, critical temperature, critical pressure, heat of vapourization, and specific heat [3, 8].

THE MAIN USE OF NATURAL GAS

Table 1: Typical natural gas analysis

	Well No. 1	Well No. 2	Well No. 3
Component	Mol percent	Mol percent	Mol percent
Methane	27.52	71.01	91.25
Ethane	16.34	13.09	3.61
Propane	29.18	7.91	1.37
I-Butane	5.37	1.68	0.31
n-Butane	17.18	2.09	0.44
I-Pentane	2.18	1.17	0.16
n-Pentane	1.72	1.22	0.17
Hexane	0.47	1.02	0.27
Heptanes and Heavier	0.04	0.81	2.42
Carbon dioxide	0.00	0.00	0.00
Hydrogen sulphide	0.00	0.00	0.00
Nitrogen	0.00	0.00	0.00
Total	100.00	100.00	100.00

Note: Production from many wells will contain small quantities of CO_2, H_2S, and N_2

Due to the variety of natural gas constituents, it finds wide application either as an energy source or as feedstock to the chemical/petrochemical industries, etc;

i. As an energy source- Natural gas competes with petroleum products, notably fuel oil,

diesel and liquefied petroleum gas (LPG). It is less expensive, burns cleaner and is more abundant than all these other fuels.

ii. As a feedstock to chemical and petrochemical industries- Natural gas and natural gas liquids are used to manufacture a gamut of intermediate chemicals and finished products such as ammonia, oxoalcohols, chloromethanes, methanol, fertilizer, etc.
iii. As a residential fuel- In temperate countries because of the climatic conditions, a sizeable gas market exists in the distribution of natural gas for domestic heating and cooking, and for refrigeration and air conditioning.

PETROCHEMICALS FROM NATURAL GAS (METHANE)

The preparation of chemicals and chemical intermediates from natural gas should not be restricted to those described here but should be regarded as some of the building blocks of the petrochemical industry. Methane is the major constituent of natural gas (95 to 98%) [1, 3, 4, 5]. Petrochemical processes begin with relatively few basic raw materials, expand into a complex of network of chemicals and converge to materials that serve specific functions as consumer products [1]. The raw material base for the petrochemical industry primarily depends upon the types of intermediates and final products required by industry and consumer. Almost all petrochemicals are derived from three sources:

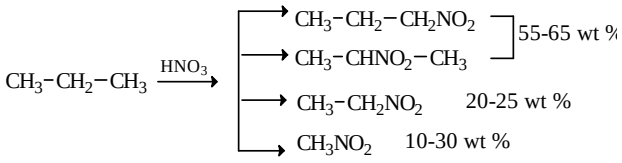
1.) Carbon monoxide/hydrogen (synthesis gas, syn gas) from reforming natural gas (methane)
2.) Olefins from pyrolysis of ethane, propane-butane (LPG, LP-gas) or distillates.
3.) Aromatics from catalytic reforming.

The three main sources for petrochemicals lead to products which are marketable items in their own right, as well as raw materials for a great many other petrochemicals used both as intermediates and as finished products. One man's product is often another man's raw material. For example, a producer of basic petrochemicals could consider methane (natural gas) as his only raw material and synthesis gas (CO/H_2), after conversion to methanol, as his finished product. An intermediate producer uses the merchant methanol as raw material to produce formaldehyde as a finished product while a resin manufacturer would see the formaldehyde as a basic raw material for the production of phenolformaldehyde resins.

In spite of its small size, methane is the precursor of a wide variety of compounds as shown in figure 1 [2]. It is not easy, however, first the molecule must be rent asunder and then reformed into useful products such as methanol, formaldehyde, ammonia and urea. The transformation of methane into these compounds is effected through synthesis gas, which may come from many other sources other than methane.

ETHANE

Ethane, like methane, has its relationship with petrochemicals primarily through a single product. With methane it is synthesis gas, $CO + H_2$, and with ethane, it is ethylene, $CH_2=CH_2$. Ethane is the most desirable feedstock for ethylene production when a minimum amount of by-product is desired. The direct conversion of ethane to vinyl chloride is the only other process currently in use for the production of a petrochemical from ethane.



PROPANE

Propane is more versatile than ethane as a feedstock for petrochemicals. This is at least partly caused by the presence of the more reactive secondary hydrogen atoms in the molecule.

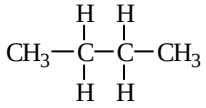
The two types of hydrogen, however, cause isomer problems in substitution reactions as illustrated in the production of nitropropanes. The *nitration* of propane has been limited industrially primarily because the product is a complex mixture. Not only are both possible substitution products formed but also carbon-carbon fission products are formed as well.

The nitropropanes are good solvents and nitromethane has been used as an additive in fuels used in racing cars. Nitropropanes react with formaldehyde to produce nitroalcohols.

$$CH_3\text{-}CH_2\text{-}CH_2NO_2 + HCHO \rightarrow CH_3\text{-}CH_2\text{-}CHNO_2\text{-}CH_2OH$$

These difunctional compounds are versatile solvents but expensive.

N-BUTANE



n-Butane is obtained from natural gas, refinery streams (from hydrocrackers), and imports. The major utilization of n-butane, over 500,000 bpd, [1] is to control vapour pressure of gasoline.

n-Butane has been the main feedstock for the production of butadiene by dehydrogenation process. This source is being replaced by steam cracking for ethylene, which produces considerable butadiene as a byproduct.

The chemistry of n-butane is more varied than that of propane, partly because n-butane has four secondary hydrogen atoms and three carbon-carbon bonds that can be broken.

Other than for the production of ethylene and butadiene, the chemical utilization involves its oxidation to various organic acids, aldehydes, ketones, alcohols and esters; usually in complex mixtures.

SYNTHESIS GAS

Synthesis gas is a mixture of carbon monoxide (CO) and hydrogen (H_2) that forms the beginning of a wide range of chemicals Fig 2. The production of synthesis gas, i.e., mixtures of carbon monoxide and hydrogen has been known for several centuries. But it is only with the commercialization of the Fischer-Tropsch reaction that the importance of synthesis gas was realized [2, 8].

INORGANIC PETROCHEMICALS

Although the focus of this text is the organic chemistry of petroleum gas and its derivatives, mention should be made of the inorganic petrochemical products. Thus, an inorganic petrochemical is one that does not contain carbon atoms; typical examples are sulphur (S), ammonium sulphate [$(NH_4)_2SO_4$], ammonium nitrate (NH_4NO_3), and nitric acid (HNO_3).

Of the inorganic petrochemicals, ammonia is by far the most common. Ammonia is produced by the direct reaction of hydrogen with nitrogen, with air being the source of nitrogen:

$$N_2 + 3H_2 \rightarrow 2NH_2$$

Ammonia production requires hydrogen from a hydrocarbon source. Traditionally, the hydrogen was produced from a coke and steam reaction [2], but refinery gases, steam reforming of natural gas (methane) and naphtha streams, and partial oxidation of hydrocarbons or higher-molecular-weight refinery residual materials (residua, asphalt) are sources of hydrogen. The ammonia is used predominantly for the production of ammonium nitrate (NH_4NO_3) as well as other ammonium salts and urea (H_2HCONH_2) which are major constituents of fertilizers.

Carbon black is made predominantly by the partial combustion of carbonaceous (organic) material in a limited supply of air. The carbonaceous sources vary from methane to aromatic petroleum oils to coal tar byproducts. The carbon black is used primarily in the production of synthetic rubber.

Sulphur, another inorganic petrochemical, is obtained by the oxidation of hydrogen sulphfide:

$$H_2S + O_2 = H_2O + S$$

Hydrogen sulphide is a constituent of natural gas and also of the majority of refinery gas streams, especially those off-gases from hydrodesulphurization processes. A large majority of the sulphur is converted to sulphuric acid for the manufacture of fertilizers and other chemicals. Other uses for sulphur include the production of carbon disulphide, refined sulphur, and pulp and paper industry chemicals.

CHALLENGES AND PROSPECTS

In order to promote gas utilization as industrial raw material, the Federal Government of Nigeria should establish more gas – based industries. At present only the National Fertilizer Company (NAFCON) fertilizer plant at Onne, Rivers state and the Nigerian National Petroleum Corporation (NNPC) petrochemical plants, use the natural gas as feedstock. The other gas – based industries e.g. Aluminium Smelter Company of Nigeria (ALSCON), Delta Steel, Ajaokuta Steel etc. only utilize the gas as energy source. Apart from the above gas – based projects, the NNPC was vigorously pursuing plans for the establishment of industrial outfits for the production of methanol and methyl – tertiary – butyl ether (MTBE) [9]. The MTBE is useful for increasing the octane value of gasoline. The

establishment of these two projects will definitely add value to our gas resources for optimal utilization and job creation. Unfortunately and very sad, for over a decade now, this Methanol – MTBE project has not been executed. The NAFCON phase II and III projects which would have been very vital for national growth, employment opportunity and gas – based has also been put aside.

So as it can be inferred from the foregoing, there are prospects for natural gas utilization as industrial raw material for the chemical, petrochemical and allied industries.

CONCLUSION

In summary natural gas (methane) can be a very important source of petrochemical feedstock for the production of intermediate and finished goods. It can be used as a source of hydrocarbons (e.g. ethane and propane) that are higher in molecular weight than methane and that are important chemical intermediates.

Nigeria is richly blessed with natural gas reserves. This God – given resource should be maximally utilized

both as energy source and as a feedstock for gas – based industries. There are various chemicals/petrochemicals that can be produced from natural gas. The Federal Government, private sector and well to do Nigerians should invest in gas – based industries. The sale of LNG is good, but the money earned from it should be invested in gas – based industries to create job opportunities for Nigerians.

REFERENCE

1. L.F. Hatch, S. Matar (1982). "From Hydrocarbons to Petrochemicals". Gulf Publishing Co. Book Division, Houston,
2. J.G. Speight (1999). "The Chemistry and Technology of Petroleum. 3rd ed., Revised and Expanded. Marcel Dekker, Inc.
3. "Field Handling of Natural Gas" 3rd Ed. Petroleum Extension Service. University of Texas at Austin, Austin. 1972.
4. Lebedev, N.N. (1984). "Chemistry and Technology of Basic Organic and Petrochemical Synthesis". Vol. I Mir Publishers Moscow.
5. NNPC manual on "Natural Gas and its uses".
6. B. Buckley (2003) "Lead paper presented by GM Nigeria LNG at the 33rd Conference/AGM of Nigerian Society of Chemical Engineers at Gateway Hotel, Abeokuta".
7. K. Van Dyke (1997). "Fundamentals of Petroleum". 4th Edition. Petroleum Extension Service. University of Texas at Austin, Austin.
8. Erikh, V.N.; Rasina, M.G.; Rudin, M.G. (1988). "The Chemistry and Technology of Petroleum and Gas. Mir Publishers Moscow.
9. C.C. Uzukwu (1999). "Natural Gas Utilization in Nigeria" Nigerian Society of Chemical Engineers Proceedings of the 29th Annual Conference/AGM, Port-Harcourt.