

PETROLEUM: CHEMISTRY, REFINING, FUELS AND PETROCHEMICALS - PETROCHEMICALS

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Summary

Petrochemicals is any of a large group of chemicals manufactured from petroleum and natural gas as distinct from fuels and other products, derived from petroleum and natural gas by a variety of processes and used for a variety of commercial purposes (Chenier, 1992; Meyers 2005,; Speight, 2007; Naderpour, 2008).

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.

It is the changes in product demand that have been largely responsible for the evolution of the petroleum industry from the demand for asphalt mastic used in ancient times to the current high demand for gasoline, other liquid fuels and products as well increasing demand for a wide variety of petrochemicals.

1. Introduction

Petrochemicals are generally considered chemical compounds derived from petroleum either by direct manufacture or indirect manufacture as by-products from the variety of processes that are used during the refining of petroleum. Gasoline, kerosene, fuel oil, lubricating oil, wax, asphalt, and the like are excluded from the definition of petrochemicals, since they are not, in the true sense, chemical compounds but are in fact intimate mixtures of hydrocarbons.

Processes such as coking or visbreaking processes a variety of gases is produced. Another group of refining operations that contributes to gas production is that of the *catalytic cracking processes*. Both catalytic and thermal cracking processes result in the formation of unsaturated hydrocarbons, particularly ethylene ($\text{CH}_2=\text{CH}_2$), but also propylene (propene, $\text{CH}_3\text{CH}=\text{CH}_2$), *iso*-butylene [*iso*-butene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$] and the *n*-butenes ($\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$, and $\text{CH}_3\text{CH}=\text{CHCH}_3$) in addition to hydrogen (H_2), methane (CH_4) and smaller quantities of ethane (CH_3CH_3), propane ($\text{CH}_3\text{CH}_2\text{CH}_3$), and butanes [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $(\text{CH}_3)_3\text{CH}$]. Diolefins such as butadiene ($\text{CH}_2=\text{CHCH}=\text{CH}_2$) and are also present. A further source of refinery gas is *hydrocracking*, a catalytic high-pressure pyrolysis process in the presence of fresh and recycled hydrogen. The feedstock is again heavy gas oil or residual fuel oil, and the process is mainly directed at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again have to be separated into lighter and heavier streams; any surplus recycle gas and the liquefied petroleum gas from the hydrocracking process are both saturated.

The composition of the process gas varies in accordance with reforming severity and reformer feedstock. All catalytic reforming processes require substantial recycling of a hydrogen stream. Therefore, it is normal to separate reformer gas into a propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) and/or a butane stream [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ plus $(\text{CH}_3)_3\text{CH}$], which becomes part of the refinery liquefied petroleum gas production, and a lighter gas fraction, part of which is recycled. In view of the excess of hydrogen in the gas, all products of catalytic reforming are saturated, and there are usually no olefin gases present in either gas stream.

The refinery gas (or the process gas) stream and the products of naphtha cracking are the source of a variety of *petrochemicals*. Thus, petrochemicals are chemicals derived from petroleum and natural gas and, for convenience of identification, petrochemicals can be divided into two groups: (1) primary petrochemicals and (2) intermediates and derivatives.

Primary petrochemicals include: olefins (ethylene, propylene and butadiene) aromatics (benzene, toluene, and xylenes); and methanol. *Petrochemical intermediates* are generally produced by chemical conversion of primary petrochemicals to form more complicated derivative products.

The petrochemical industry has grown with the petroleum industry and is considered by

some to be a mature industry. However, as is the case with the latest trends in changing crude oil types, it must also evolve to meet changing technological needs. The manufacture of chemicals or chemical intermediates from a variety of raw materials is well established. And the use of petroleum and natural gas is an excellent example of the conversion of such raw materials to more valuable products. The individual chemicals made from petroleum and natural gas are numerous and include industrial chemicals, household chemicals, fertilizers, and paints, as well as intermediates for the manufacture of products, such as synthetic rubber and plastics.

The main objective in producing chemicals from petroleum is the formation of a variety of well-defined chemical compounds that are the basis of the petrochemical industry. It must be remembered, however, that ease of separation of a particular compound from petroleum does not guarantee its use as a petrochemical building block. Other parameters, particularly the economics of the reaction sequences, including the costs of the reactant equipment, must be taken into consideration.

2. Chemicals from Paraffins

It is generally true that only paraffin hydrocarbons from methane (CH₄) through propane (C₃H₈) are used as starting materials for specific chemical syntheses (Chenier, 1992). This is because the higher members of the series are less easy to fractionate from petroleum in pure form, and also because the number of compounds formed in each particular chemical treatment makes the separation of individual products quite difficult.

2.1. Halogenation

The ease with which chlorine can be introduced into the molecules of all the hydrocarbon types present in petroleum has resulted in the commercial production of a number of widely used compounds. With saturated hydrocarbons the reactions are predominantly substitution of hydrogen by chloride and are strongly exothermic, difficult to control, and inclined to become explosively violent:



Moderately high temperatures are used, about 250 to 300°C (480 to 570°F) for the thermal chlorination of methane, but as the molecular weight of the paraffin increases the temperature may generally be lowered. A mixture of chlorinated derivatives is always obtained, and many variables, such as choice of catalyst, dilution of inert gases, and presence of other chlorinating agents (antimony pentachloride, sulfuryl chloride, and phosgene), have been tried in an effort to direct the path of the reaction.

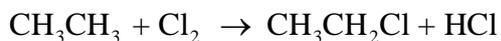
Methane yields four compounds upon chlorination in the presence of heat or light:



These compounds, known as chloromethane or methyl chloride, dichloromethane or methylene chloride, trichloromethane or chloroform, and tetrachloromethane or carbon

tetrachloride, are used as solvents or in the production of chlorinated materials.

Other examples of the chlorination reaction include the formation of ethyl chloride by the chlorination of ethane:



Ethyl chloride ($\text{CH}_3\text{CH}_2\text{Cl}$) is also prepared by the direct addition of hydrogen chloride (HCl) to ethylene ($\text{CH}_2=\text{CH}_2$) or by reacting ethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) or ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) with hydrogen chloride. The chlorination of *n*-pentane and *iso*-pentane does not take place in the liquid or vapor phase below 100°C (212°F) in the absence of light or a catalyst, but above 200°C (390°F) it proceeds smoothly by thermal action alone. The hydrolysis of the mixed chlorides obtained yields all the isomeric amyl (C_5) alcohols except *iso*-amyl alcohol. Reaction with acetic acid produces the corresponding amyl acetates, which find wide use as solvents.

2.2. Nitration

Hydrocarbons that are usually gaseous (including normal and *iso*-pentane) react smoothly in the vapor phase with nitric acid to give a mixture of nitro-compounds, but there are side reactions, mainly of oxidation. Only mononitro-derivatives are obtained with the lower paraffins as high temperatures, and they correspond to those expected if scission of a C-C and C-H bond occurs.

Ethane, for example, yields nitromethane and nitroethane,



Propane yields nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane:

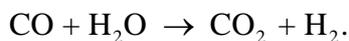
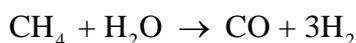
The nitro-derivatives of the lower paraffins are colorless and non-corrosive and are used as solvents or as starting materials in a variety of syntheses. For example, treatment with inorganic acids and water yields fatty acids (RCO_2H) and hydroxylamine (NH_2OH) salts and condensation with an aldehyde ($\text{RCH}=\text{O}$) yields nitroalcohols [$\text{RCH}(\text{NO}_2)\text{OH}$].

2.3. Oxidation

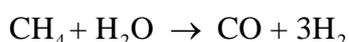
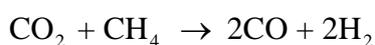
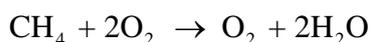
The oxidation of hydrocarbons and hydrocarbon mixtures has received considerable attention, but the uncontrollable nature of the reaction and the mixed character of the products have made resolution of the reaction sequences extremely difficult.

Therefore it is not surprising that, except for the preparation of mixed products having specific properties, such as fatty acids, hydrocarbons higher than pentanes are not employed for oxidation because of the difficulty of isolating individual compounds.

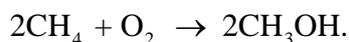
Methane undergoes two useful reactions at 90°C (195°F) in the presence of iron oxide (Fe₃O₄) as a catalyst:



Alternatively, partial combustion of methane can be used to provide the required heat and steam. The carbon dioxide produced then reacts with methane at 900°C (1650°F) in the presence of a nickel catalyst:



Methanol (methyl alcohol, CH₃OH) is the second major product produced from methane. Synthetic methanol has virtually completely replaced methanol obtained from the distillation of wood, its original source material. One of the older trivial names used for methanol was wood alcohol. The synthesis reaction takes place at 350°C and 4,500 psi in the presence of ZnO as a catalyst:

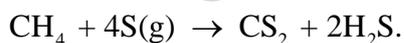


Most of the methanol is then oxidized by oxygen from air to formaldehyde, (sometimes referred to as methanal):



Formaldehyde is used to produce synthetic resins either alone or with phenol, urea, or melamine; other uses are minor.

By analogy to the reaction with oxygen, methane reacts with sulfur in the presence of a catalyst to give the carbon disulfide used in the rayon industry:



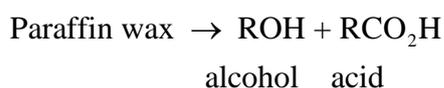
The major non-petrochemical use of methane is in the production of hydrogen for use in the Haber synthesis of ammonia. Ammonia synthesis requires nitrogen, obtained from air, and hydrogen. The most common modern source of the hydrogen consumed in ammonia production, about 95% of it, is methane.

When propane and butane are oxidized in the vapor phase, without a catalyst, at 270 to 350°C (520 to 660°F) and at 50 to 3000 psi, a wide variety of products is obtained, including C₁ to C₄ acids, C₂ to C₇ ketones, ethylene oxide, esters, formals, acetals, and

others.

Cyclohexane is oxidized commercially and is somewhat selective in its reaction with air at 150 to 250°C (300 to 480°F) in the liquid phase in the presence of a catalyst, such as cobalt acetate. Cyclohexanol derivatives are the initial products, but prolonged oxidation produces adipic acid. On the other hand, oxidation of cyclohexane and methylcyclohexane over vanadium pentoxide at 450 to 500°C (840 to 930°F) affords maleic and glutaric acids.

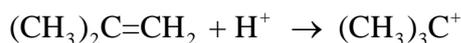
The preparation of carboxylic acids from petroleum, particularly from paraffin wax, for esterification to fats or neutralization to form soaps has been the subject of a large number of investigations. Wax oxidation with air is comparatively slow at low temperature and normal pressure, very little reaction taking place at 110°C (230°F), with a wax melting at 55°C (130°F) after 280 h. At higher temperatures the oxidation proceeds more readily; maximum yields of mixed alcohol and high-molecular-weight acids are formed at 110 to 140°C (230 to 285°F) at 60 to 150 psi; higher temperatures (140 to 160°C, 285 to 320°F) result in more acid formation:



Acids from formic (HCO₂H) to that with a 10-carbon atom chain [CH₃(CH₂)₉CO₂H] have been identified as products of the oxidation of paraffin wax. Substantial quantities of water-insoluble acids are also produced by the oxidation of paraffin wax, but apart from determination of the average molecular weight (ca. 250), very little has been done to identify individual numbers of the product mixture.

2.4. Alkylation

Alkylation chemistry contributes to the efficient utilization of C₄ olefins generated in the cracking operations and the products make valuable contribution to the motor gasoline octane pool. *Iso*-butane has been added to butenes (and other low-boiling olefins) to give a mixture of highly branched octanes (e.g., heptanes) by a process called alkylation. The reaction is thermodynamically favored at low temperatures (<20°C), and thus very powerful acid catalysts are employed. Typically, sulfuric acid (85 to 100%), anhydrous hydrogen fluoride, or a solid sulfonic acid is employed as the catalyst in these processes. The first step in the process is the formation of a carbocation by combination of an olefin with an acid proton:



Step 2 is the addition of the carbocation to a second molecule of olefin to form a dimer carbocation. The extensive branching of the saturated hydrocarbon results in high octane. In practice, mixed butenes are employed (*iso*-butylene, 1-butene, and 2-butene), and the product is a mixture of isomeric octanes that has an octane number of 92 to 94.

3. Chemicals from Olefins

Olefins (C_2H_{2n}) are the basic building blocks for a host of chemical syntheses (Chemier, 1992). These unsaturated materials enter into polymers, and rubbers and with other reagents react to form a wide variety of useful compounds, including alcohols, epoxides, amines, and halides.

Ethylene manufacture via the steam cracking process is in widespread practice throughout the world. The operating facilities are similar to gas oil cracking units, operating at temperatures of $840^\circ C$ ($1550^\circ F$) and at low pressures (24 psi). Steam is added to the vaporized feed to achieve a 50-50 mixture, and furnace residence times are only 0.2 to 0.5 second. Ethane extracted from natural gas is the predominant feedstock for ethylene cracking units. Propylene and butylene are largely derived from catalytic cracking units and from cracking a naphtha or light gas oil fraction to produce a full range of olefin products.

Virtually all propene or propylene is made from propane, which is obtained from natural gas stripper plants or from refinery gases:



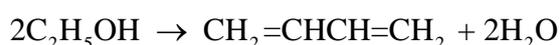
The uses of propene include gasoline (80%), polypropylene, iso-propanol, trimers, and tetramers for detergents, propylene oxide, cumene, and glycerin.

Two butenes or butylenes (1-butene, $CH_3CH_2CH=CH_2$, and 2-butene, $CH_3CH=CHCH_3$) are industrially significant. The latter has end uses in the production of butyl rubber and polybutylene plastics. On the other hand, 1-butene is used in the production of 1,3-butadiene ($CH_2=CHCH=CH_2$) for the synthetic rubber industry. Butenes arise primarily from refinery gases or from the cracking of other fractions of crude oil.

Butadiene can be recovered from refinery streams as butadiene, as butenes, or as butanes; the latter two on appropriate heated catalysts dehydrogenate to give 1,3-butadiene:



An alternative source of butadiene is ethanol, which on appropriate catalytic treatment also gives the compound di-olefin:



Olefins containing more than four carbon atoms are in little demand as petrochemicals and thus are generally used as fuel. The single exception to this is 2-methyl-1,3-butadiene or isoprene, which has a significant use in the synthetic rubber industry. It is more difficult to make than is 1,3-butadiene. Some is available in refinery streams, but

more is manufactured from refinery stream 2-butene by reaction with formaldehyde:



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Biographical Sketch

Dr. Speight has more than thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research and development in refining heavy oil and coal, and related environmental issues. He has well over four hundred publications, reports, and presentations detailing these research activities and has taught more than forty related courses.

Dr. Speight is currently editor of the journal *Petroleum Science and Technology* (formerly *Fuel Science and Technology International*) and editor of the journal *Energy Sources*. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemical and Fuels Engineering at the University of Utah.

Dr. Speight is the author/editor/compiler of more than twenty books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, for Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996 for his Contributions to Coal Research. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia for Exceptional Work in Petroleum Science in 1997. In 2001, Dr. Speight was also awarded the Einstein Medal of the Russian Academy of Sciences (Natural) in recognition of Outstanding Contributions and Service in the field of Geologic Sciences.