PETROCHEMICALS

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Summary

Carbon and hydrogen are important components in many industrial chemicals, and their abundance in the form of natural gas and petroleum meant that the petrochemical industry rapidly developed in the mid to late 20^{th} Century as an increasing number of chemical discoveries were made. Hence petrochemicals in the form of plastics, synthetic fibers, synthetic rubbers, resins, fertilizers etc. are important materials in producing all sorts of useful products in modern life.

The development of chemical engineering as a discipline is strongly linked to the petrochemicals industry. Innovations in catalysis, unit operations such as reactor technology and distillation, and heat integration were driven by an increasing number of products and competition to develop alternative and more energy efficient chemical processes.

This chapter provides a brief introduction to petrochemicals and some of the more important chemical processes.

1. Introduction

Many industrial chemicals contain carbon and hydrogen as their major components. Up until the 1920's the raw materials used for their production was principally coal or fermentation products. Thermal cracking to make gasoline yielded olefins as a by-product and it was realized that these could be treated to produce useful chemicals. The petrochemical industry developed rapidly in the USA between the First and Second World Wars with the building of oil refineries and access to natural gas. The Second World War provided a stimulus for further development of the industry in the USA. These developments led to rapid growth in the range of products being manufactured with petroleum becoming an important source of alcohols, plastics, rubbers and solvents. The European petrochemical industry was established in the 1950's with commissioning of crackers next to crude oil refineries. Whereas in the USA most of the petrochemicals industry utilized gaseous feedstocks, Europe and the rest of the world used liquid feedstocks in the form of naphtha which was in excess due to the lower demand for gasoline.

Petrochemicals, chemicals derived from petroleum, are used in the manufacture of a vast array of products such as synthetic textiles, fibers, plastics, rubbers, solvents, alcohols and fertilizers.

The development of the petrochemicals industry, to manufacture this wide variety of materials, firmly established the discipline of chemical engineering in the design and operation of chemical processes, by contributing to the further development of unit operations to achieve desired processing steps. The production of petrochemicals requires the transformation of the raw materials found in crude oil and natural gas by means of chemical reactions followed by the separation of unreacted and by-products from the desired products. A diverse range of chemical reaction routes have been exploited which required innovations in catalysis and reactor technology. The separation and purification of the final products also required developments in distillation, solvent extraction and physical separation processes. Petrochemical process plants tend to be large scale and continuous processes. Hence, large quantities of heat are generated and consumed by various unit operations. In order to improve the energy efficiency and hence reduce costs, heat integration techniques were developed and utilized to exchange heat between process streams and to generate steam from excess heat e.g. in reactors thus reducing the demand on utilities. Furthermore, there is often large scale integration of petrochemical process plants to enable the most efficient use of products and by-products as intermediates and feedstocks in one location. This enables economies of scale to be exploited and minimizes costs such as transportation.

The full range of products and the chemical processes employed in their manufacture is too diverse to cover in a single chapter so this will focus on major routes from raw materials to important intermediates from which there are many derivative products.

2. Petrochemicals Overview

The petrochemical business tends to be broken up into "value chains" with a progression from raw materials to intermediates manufacture followed by derivatives production. They are termed "value chains" because at each stage of manufacture the chemicals are modified through reactions to produce higher value products and these products follow a logical sequence of processes. Additional value can be added at each stage by reducing the costs of energy supply, transport, etc. hence petrochemical plants tend to be co-located and are highly integrated with products and by-products flowing between plant and company boundaries. There are often several routes to producing a chemical from the same raw material which differ in reaction conditions, reactor design, type of catalyst, separation processes etc. These processes are developed by companies following extensive research. Hence, each individual chemical process utilized to manufacture petrochemicals is usually a licensed technology, to which companies own the rights of use.

Two major groups of petrochemicals are derived from crude oil and natural gas – olefins and aromatics. These constitute the primary intermediates which are the building blocks of many derivatives which become final consumer products. Natural gas is also used to produce synthesis gas from which methanol and ammonia can be produced.

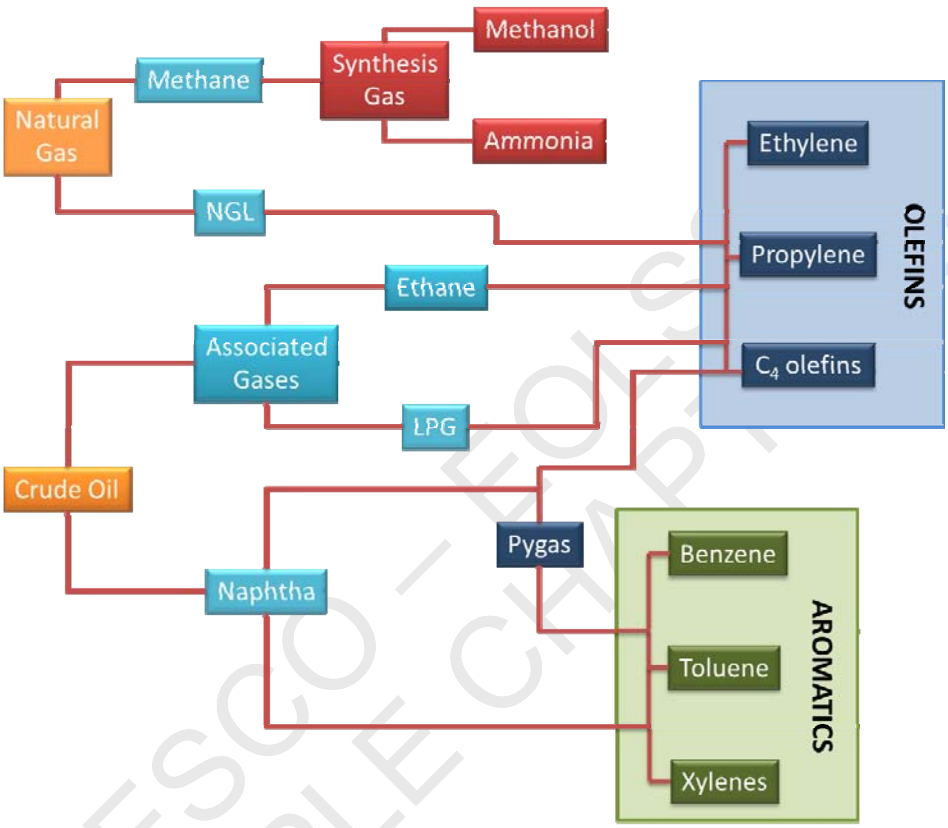

Figure 1. Primary petrochemical intermediates pathways

3. Olefins

Olefins are unsaturated hydrocarbon molecules containing one or more double-bonded carbon-carbon linkages. These linkages can be usefully exploited for subsequent chemical operations which are why olefins are some of the most important intermediates in the petrochemicals industry.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_2\text{=}CH\text{-}CH_2\text{-}CH_3 \longrightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2$$

n-butane — butene-1 — butadiene-1,3

Figure 2. Dehydrogenation of butane

Olefins are produced by removing hydrogen from saturated hydrocarbon molecules. An example showing the conversion of *n*-butane to butene-1 and then to butadiene-1,3 is shown in Figure 2.

The most useful and hence desirable olefins are ethylene, propylene, butenes and butadiene. These can be manufactured by cracking a variety of feedstocks such as ethane and propane extracted from natural gas, or naphtha and gas oils produced from refining crude oil. Feedstock is pre-heated and introduced to cracking furnaces where it is mixed with high pressure steam.

These furnaces have a very short residence time ~0.1 seconds and the temperature is raised to 650°C – 850°C. The furnace products are then rapidly quenched to prevent olefins reacting with one another.

Methane and hydrogen are extracted in the chilling train before the olefin products (ethylene, propylene, butenes and butadiene) are separated by fractionation. Further separation of C_4s from one another requires solvent extraction. By-products such as propane can be recycled to improve the olefin yield. The other major by-product is typically an aromatics rich gasoline (pyrolysis gasoline, “pygas”).

The yields and relative proportions of olefins produced in this process are governed by feedstock and the cracking conditions. For example, an ethane feedstock will yield >80 wt.% ethylene whereas a naphtha will yield 30 – 35 wt.% ethylene.

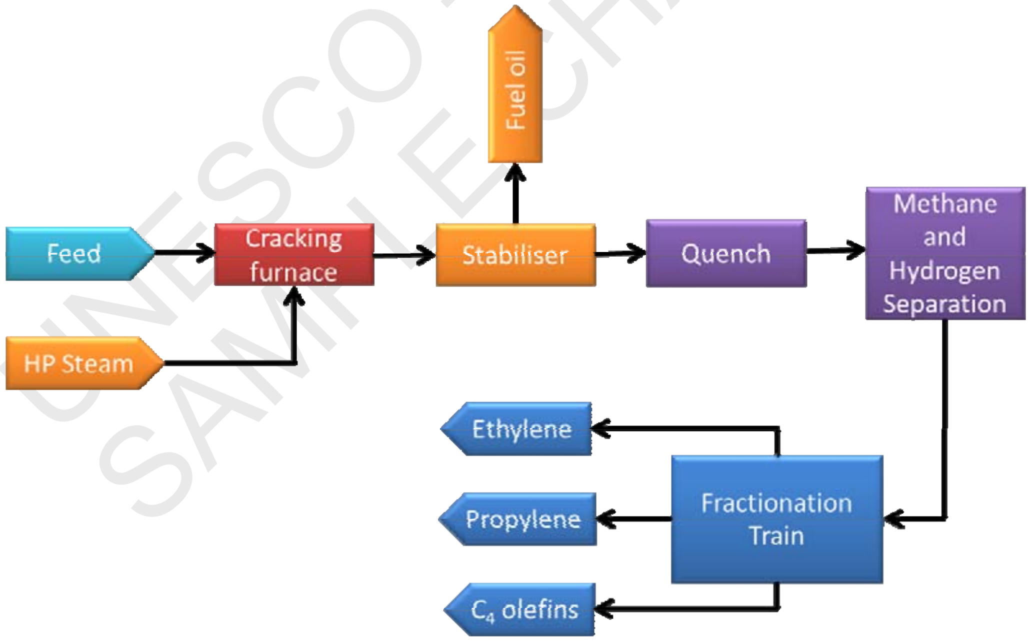

Figure 3. Olefins production process

The olefins produced by this process are of high purity and undergo further transformations to convert them to consumer products. Some of the more common uses are illustrated in the tables below.

Ethylene Derivatives	**Uses**
Polyethylene	Films, moldings, pipes, cable covering etc.
Ethylene oxide	Intermediate for: ethylene glycol (anti-freeze, desiccant), polyester, detergents
Styrene	Polystyrene plastics, synthetic rubber
Ethyl alcohol	Solvent, chemical intermediate
Acetaldehyde	Produces acetic acid which in turn is used to produce poly-vinyl acetate (PVA) adhesives, cellulose acetate fibers and plastics, plasticizer alcohols, paint resin intermediates
Ethylene dichloride	Produces vinyl chloride which in turn is converted to poly-vinyl chloride (PVC) plastics

Table 1. Ethylene uses

Propylene Derivatives	**Uses**
Polypropylene	Films, fibers and plastic moldings
Propylene oxide	Intermediate for plastic foams (e.g. polyurethane)
Acetone	Solvent
Butanol	Solvent
Acrylic acid	Intermediate for adhesives, flocculants, detergents, varnishes
Acrylonitrile	Acrylic fibers and intermediate for nylon
Ethyl hexanol	Solvent, manufacture of plasticizers
Cumene	Raw material for manufacture of acetone (solvent), phenol (intermediate for resins)

Table 2. Propylene derivatives and their uses

C_4 Olefins	**Uses**
Butadiene	
Nitrile-butadiene-rubber (NBR)	Synthetic rubbers
Styrene-butadiene-rubber (SBR)	Synthetic rubbers
iso-butene	
Butyl rubber	(tyre inner tubes), lube oil additives
Methy-tert-butyl-ether (MTBE)	Oxygenates for fuel
n-butenes	
Butanol	Solvent
Methyl ethyl ketone	Solvent and lube oil dewaxing agent
Higher olefins	Up to 20 carbon atoms for use as plasticizers,

Table 3. C_4 olefins uses

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Biographical Sketch

Colin Deddis is a Chartered Engineer and Fellow of the Institution of Chemical Engineers, with over 20 years experience, predominantly in the oil and gas industry. He began his career with BP in oil refining and gas processing supporting operations and brownfield projects before moving into BPs upstream business where he has held positions supporting offshore production operations and as a lead process engineer on major projects. In the last several years he worked as a lecturer in Chemical Engineering Design at the University of Cambridge before moving back into the oil industry as an engineering consultant prior to rejoining BP in 2007. Colin is currently a Senior Process Engineer working in BPs Exploration and Production Technology Group. In this role he provides internal technical services to major projects and operations and is involved in technology development in the areas of separation and sand management.