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THERMAL PROCESSING OF HYDROCARBONS

PETROLEUM TO PETROCHEMICALS

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Petroleum to petrochemicals

6.1 Basic definition

Petrochemicals are the hydrocarbon materials derived from crude oil that are used for the manufacture of specific organic compounds other than the fuel. The most common petrochemicals are "olefins" and "aromatics," which are used for the manufacture of plastics, solvents, or chemicals. The most high-value olefins are ethylene, propylene, butenes, iso-butenes, butadienes, and iso-prenes. The corresponding high-value aromatics are benzene, toluene, ethylbenzene, xylene (BTEX), and styrene.

6.2 Introduction

Things are moving so fast that by the time this book is published, a lot of things may have changed. In this digital age, things are moving at the speed of light. The purpose of this sub-chapter is to make the readers aware of the situation and prepared to face the future.

According to the recent forecasts released by several energy news outlets[1], natural gas will take over as the main fossil fuel, over solid or liquid hydrocarbons, by 2040. The US is expected to dominate the energy market beyond 2020 with increased tight oil/tight gas production and a secure supply of natural gas to satisfy global demand. Given the impact of climate change, we are heading towards a global energy transition with natural gas playing an important role. Whether it is in the form of natural gas, or compressed gas (as CNG) or liquefied gas (as LNG), global cooperation and partnerships are attracting international investments[1].

Nevertheless, market demand and economics dictate the pathway the industry would like to follow. Refineries are now looking for an alternative as they are facing a lower profit margin in transportation fuel. Due to the surge in polymer consumer demand, important global players are now focusing on petrochemicals more than ever to narrow the gap or shortage of plastics in the expanding electronics industry.

As per several publications in the O&GJ during the summer of 2018, petrochemicals are becoming the fastest growing sector in the petroleum industry. They see a significant increase in investment for future development of the downstream industry in the Middle East. The name of the game is now "digital transformation," where the focus is customer-oriented—identifying and exploring the opportunities and providing support. Saudi Aramco is leading the way by introducing a game-changing project called "Crude-oil-to-chemicals," implemented jointly with SABIC. It is a massive undertaking, using first-of-its-kind technology developed internally, resulting in a product that is less expensive to produce with a much lower carbon footprint.

O&GJ (October 2018) further confirmed that Saudi Aramco and Total SA have signed an agreement to launch a front-end engineering design (FEED) for their previously announced proposal to add an integrated petrochemical complex downstream of their jointly held Saudi Aramco Total Refinery & Petrochemicals Co.'s (Satorp) 440,000-b/d full conversion refinery in Jubail, Saudi Arabia. The new complex will include a mixed-feed steam cracker—50% ethane and refinery off gas—with a capacity to produce 1.5 million tons/year (MMTPA) of ethylene and related petrochemical units designed to yield an overall production of more than 2.7 MMTPA of high-quality chemical products.

Next in line is Oman Oil Refineries and Petroleum Industries Company (Orpic), aiming to invest in another massive $4.5 billion-dollar Liwa Plastics Industries Complex (LPIC) project to diversify their portfolio of vast natural gas resources. They are building a new polyolefin plant to convert gaseous hydrocarbons into olefins for the plastic industry.

In another part of Asia, Reliance Industries in Gujarat, India, is investing in liquid hydrocarbons. They are the major producers of ortho- and para-xylenes. Ortho-xylene is the feedstock to produce primary material for paints and fiberglass, whereas para-xylene is the feedstock for terephthalic acid used for the manufacture of polyester fibers. Reliance is also investing in a highly integrated 1.5 MMTPA ethylene cracker plant in its own refinery to produce feedstocks for polyethylene polymers.

On the other hand, as per China's state oil company news, China is also investing in a 0.6 MMTPA plant of solid fossil fuel coal (other than natural gas), utilizing clean coal technology based on gasification. In this process, coal is gasified to syngas, a mixture of carbon monoxide and hydrogen, which is further converted into monoethylene glycol, a petrochemical feedstock (see Chapter 6.6).

In other parts of Far East Asia, namely Vietnam and South Korea, it is also planned to expand the petrochemical business by investing in integrating refining and the petrochemical business. According to a report in the O&GJ (Aug 2018), Vietnam has already awarded a contract to build an ethylene plant using a mixed-feed flexible cracker, and South Korea is carrying out a feasibility study for the proposed construction of a 1.5 MMTPA steam cracker olefin plant in the Ulsan refinery. Downstream olefin facilities will produce polyethylene and polypropylene plants to meet Asia's rising demand for plastic industries.

O&GJ (July 2018) reported that ExxonMobil Chemical Co. has started up its 1.5 MMTPA ethane steam cracker at the company's integrated chemical and refining complex in Baytown, Texas. The new cracker will provide ethylene feedstock for the 650,000-tpy high-performance polyethylene plastics plant in Texas. This new ethane cracker will help meet the growing global demand for high-performance plastic products.

It is interesting to observe that the demand for ethylene increases with the increase in the global economy. According to publicly available information in an Argus Ethylene 2018 report, the actual demand for ethylene in the US increased to annual growth of 2.8%, more than the forecast due to a better economy, and it is expected to grow to about 4% for the next few years.

However, it is a challenge for the refiners to meet the demand with reasonable economic benefit. Economic evaluation of the production of olefins is highly dependent on the site-specific projects.

The most dependable factors are:

(i) availability of natural gas
(ii) cost of the feedstocks
(iii) cost of installation of a pyrolysis unit and steam cracker unit
(iv) separation of the byproducts, or purity of the final product
(v) cost of converting olefins into polymers
(vi) market demand and the cost of transportation of the feed and products

Finally, it depends on whether the final product is consumed within the same geographic area or at a distance. For example, for the US to reach the global market, the shipping costs are about 12% more as compared to the market within Asia[1].

On one hand, the availability of low-cost hydrocarbons from tight gas production has increased investment in steam cracker plants in the US. On the other hand, further East, they are concentrating on integrated steam cracker and refinery plants, with liquid hydrocarbons as feedstock.

The demand for propylene has also increased over the years and is growing at a faster rate than ethylene. Propylene is used in a wide variety of petrochemicals, such as propylene oxide, acrylonitrile, cumene, acrylic acid, etc. Polypropylene is used in the polymer industry, and its use as plastic has increased, especially in the automobile industry.

According to an International Energy Agency (IEA) forecast published in October 2018, future oil demand will increase, not due to the transportation industry but rather due to the increase in petrochemicals demand. There are wide varieties of petrochemicals such as fertilizers, plastic packaging materials, clothing, digital devices, medical equipment, detergents, and tires—besides the demand in the area of cars and airplanes. Though there is increasing interest in moving towards renewable energy, this actually creates additional demand for petrochemicals; renewable energy equipment, like solar panels, wind mill turbines, insulators, electric vehicles, batteries, etc., require plastic parts. According to the IEA report, after decades of decline, the United States has emerged as the low-cost petrochemical production place, mostly due to the tight oil revolution, and 40% of the global ethane-based petrochemical industries are now in the US. However, there are also environmental challenges with the increasing demand for the use of plastics.

6.3 Integration of refinery and petrochemical complex

Refineries are always looking for ways to increase their revenue. That's why existing refineries are looking for opportunities for integration of refinery and petrochemical industries. As discussed above in the introduction, new refineries are already building grassroots integrated complexes around the world.

However, refiners are facing increasing challenges with the increase in stringent environmental regulations. There are constant changes regarding feedstock qualities and quantities. More than ever before, refiners are facing cut-throat competition. The only way they can survive is through broadening their portfolios, maximizing their profits through process integrations, implementing new and advanced technologies, and digitizing their operations. They must maximize their target product production through multiple sources and multiple feedstocks within their refinery. Flexibility is the "name of the game" for survival in the current situation.

Figure 6.3 illustrates a snapshot of various pathways and opportunities, from the initial paraffinic feedstock in the refinery to producing olefins for the petrochemical industries, and then the various options for final plastic or polymer end-use utilization.

There are several advantages to multi-integrated plants:

i. Most importantly, a capital cost advantage—by eliminating some common units such as fractionations or furnace tubing
ii. Feedstock transportation cost—transferring feedstocks over the fence
iii. Availability of byproducts from one unit to be utilized in another plant—such as fuel gas or hydrogen
iv. Reduction of energy utilization through integration—improved efficiency
v. Manpower reduction—possible elimination of duplication of the work force

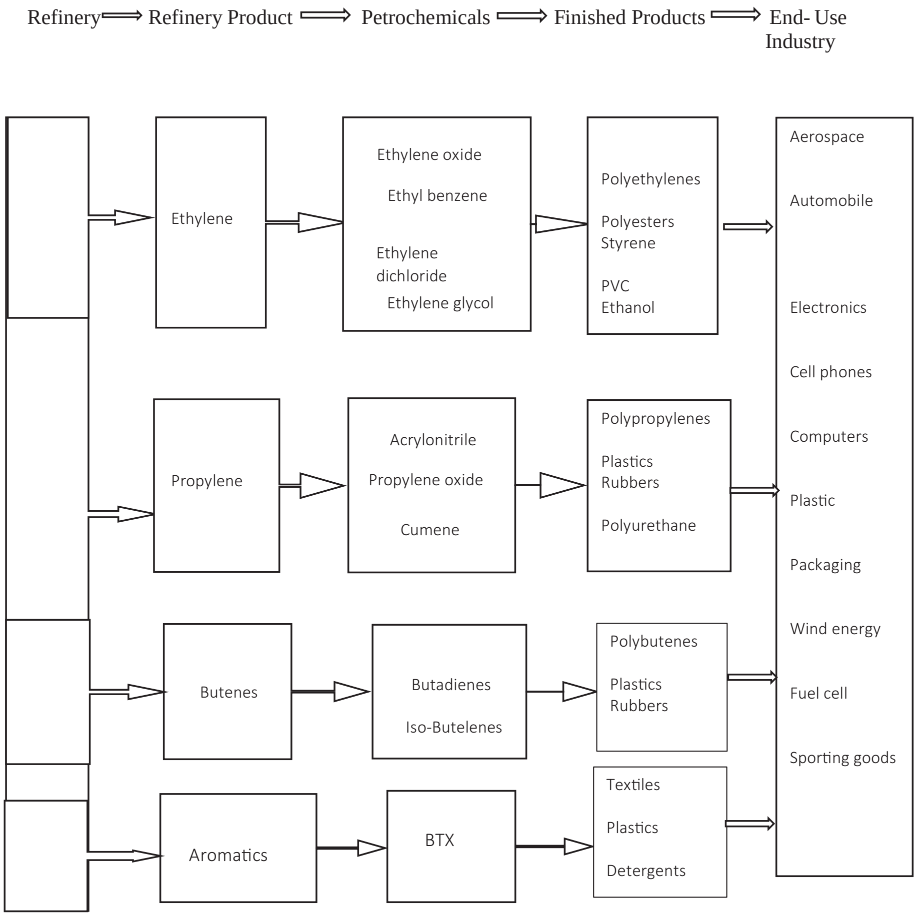

Fig. 6.3. A snapshot of the pathways from paraffinic feedstocks to the final petrochemical end products

6.4 Technologies for the production of petrochemicals

6.4.1 Background

Recently, the global petrochemical industry has grown and almost exploded due to the growing opportunities in other industries as well. Petrochemical industries have been in existence for more than a century, but recently, technological advancement has contributed dramatically in the world economy. According to several EIA reports, the chemical industry in the United States has grown to produce about half a trillion dollars' worth of products annually and to export about $100 billion of those materials. With growing worldwide populations and their increasing standard of living in all aspects of life, the demand for petroleum products is expected to increase further with no sign of slowing down. That's why this book addresses an important and timely issue for the petrochemical and energy industries.

The most challenging factor, however, is the choice of proper technology. Among the various technologies available to the manufacturer for the production of petrochemicals, it could be highlighted that the production of lower olefins through dehydrogenation of lower paraffins (C_2–C_4) may be the most suitable route for this application.

Dehydrogenation involves removal of hydrogen from saturated hydrocarbons, as follows:

$$\underset{\text{Paraffin}}{R_n\text{-}CH_2\text{-}CH_3} \quad \leftrightarrow \quad \underset{\text{Olefin}}{R_n\text{-}CH{=}CH2} \quad + \quad H2$$

where R is an alkyl group of chain length 'n' number of carbon atoms. Thus, the process is not only producing olefins but also hydrogen as a byproduct. This hydrogen can be reutilized within the refinery by recycling back to a hydrotreater or hydrocracker.

Dehydrogenation, being endothermic in nature, is quite energy-intensive. Another route available for the industry with less energy consumption is called oxidative dehydrogenation, which occurs in the presence of oxygen, as follows:

$$R_n\text{-}CH_2\text{-}CH_3 + \tfrac{1}{2}O_2 \quad \leftrightarrow \quad R_n\text{-}CH{=}CH2 \quad + \quad H2O$$

This reaction being exothermic requires less energy than the traditional dehydrogenation process, but the main problem is the strong probability of occurrence of paraffin combustion against the dehydrogenation reaction. Hence, the reaction may become uncontrollable, with the probability of an expensive shutdown.

The main source for the lower paraffinic feedstocks for the process is crude oil or natural gas. Lower hydrocarbons (C_2–C_4) are separated physically in a fractionation column inside the refinery. Cost of separation of individual hydrocarbons increases with the complexity of the mixtures and the purity of the target hydrocarbons required.

Due to the economic advantages, the energy industries are turning their investments more towards petrochemical industries than any other fields. Hence, there is also increase in continuing research activities for the development of new technologies. According to a 2018 Petrochemical report, almost one third of the chemical production technologies are based on steam cracking, and another quarter on oxidation of hydrocarbons. They are the two dominating technologies, with dehydrogenation being far behind, occupying less than 10% of the total industrial technologies.

It is becoming increasingly challenging for researchers to develop suitable catalyst to carry out the process at a minimum cost. The dehydrogenation reactions include high temperatures (above 600 °C) and mild operating pressures (below 100 psi). The catalyst normally applied to reduce the reaction temperature in dehydrogenation reactions is based on metals impregnated with alumina.

The recent increase in the production of tight gas/shale gas and the resulting increased availability of a cheap ethane source means the whole North American scenario is changing rapidly. Now, ethane is the biggest source of feedstock for ethylene production, and all steam cracker plants are switching their feedstock to ethane from naphtha. Naphtha is now available more for gasoline blends. The feedstock cost advantage is much higher in the US, as the cost of naphtha is almost three times that of ethane in equivalent mass basis.

There are 36 steam crackers in the US, out of which 33 are in the Gulf region, whereas Canada has 6, out of which 4 are in Alberta[2]. Thus, the northeastern area of Marcellus and Utica are essentially without access to any cracker plant. There is a serious shortage of pipeline for transportation. They have only two options: (i) either build a pipeline to the Gulf Coast plants, or (ii) build cracker plants in the nearby New York or Pennsylvania area. However, economics only dictates the solution, not the politics.

It should be cautioned here that the evaluation of new technologies is not an easy task. The most important factor in assessing a new technology is the "cost" of production. As this author has mentioned previously in his earlier book on heavy oil, "Economics always beats technology." Next to the cost of production comes the market value of the product. It not only depends on the market demand but also the geographical location, i.e., transportation cost. There are discussions going on for new full-scale crackers in the Eastern zone. But that needs a large-scale investment. The advantage is that it is closer to the feedstock, and it is cheaper to transport solid polymer finished product than gaseous feedstock.

There is an increasing demand for ethylene for polyethylene production. The obvious choice should be "dehydrogenation of ethane," as simple as it sounds. But even today, there is no attractive technology available that solves all the problems associated with the process. Rather, dehydrogenation of propane to propylene is much easier from the technical point of view. As has been discussed previously in Chapters 3 and 4, ethane dehydrogenation requires a higher temperature than with propane dehydrogenation. Commercial steam cracker furnace temps decrease with the increase in molecular mass of the feedstocks—for example, the "Coil outlet temperature - COT" for C_2 hydrocarbon is between 840 °–850 °C and for C_3, it is 830–840 °C, and for C_4 and higher hydrocarbons, COT is <820 °C at a steam to oil ratio of 0.35.

When the severity of the process increases, though the conversion increases, the selectivity towards ethylene formation decreases (see Figure 4.6.1), with the increase in secondary products and including fouling due to coking. If the feedstock gets heavier or for mixed feedstock, the problems with separation and the additional cost for purity of the final product also multiplies. That is the reason, though naphtha cracking sounds attractive in some parts of the world (not in the US), that due to the poor selectivity towards ethylene, high conversion naphtha cracking is not an economical solution.

Though steam cracking is popular, other technologies are also available for the production of olefins from paraffins, such as a partial-oxidation process, as discussed above. This sounds attractive over the dehydrogenation process, which is endothermic and requires heat; oxidation is exothermic and driven by the heat produced from the system itself. But this process also has its own negative points: (i) most importantly, it produces CO_2, (ii) selectivity towards olefin is lower than that of the steam cracking process, and (iii) finally, the oxidation process is difficult to control and can overshoot towards the formation of coke at any time, with shutdown of the whole plant at a very high economical penalty.

Propylene, the most popular petrochemical today, is primarily manufactured in the refinery by steam cracking or catalytic cracking of C_3 or higher molecular weight feedstocks. A steam cracker produces "polymer grade" propylene, the quality depending on the quality of the feedstock.

Petrochemicals are produced from naphtha, which is obtained after fractionation of crude oil, and then steam cracking. It would have been more favorable if they were produced directly from the crude oil itself with minimum treatment. For example, according to the author's internal studies, tight crude oil from the major US sources contains aromatic petrochemicals, such as benzene, ethylbenzene, and xylenes (no toluene). Especially the tight oil from the Permian basin consists of higher concentrations of aromatics, between 3 to 5 volume percentages of the total crude. The amounts of individual components depends on the crude oil location.

6.4.2 Crude to chemicals

It is not easy to identify the best technology for any particular process. Every project has its own unique risk, not only because of its complexities but also due to the geographical location. Risk factors also include the local environmental regulations. The best result would be to do comparative studies of various processes and to identify the impact locally (or where the product is sold).

As the demand for petrochemicals is expected to increase beyond 2020, the competition is increasing with the increase in the number of players in this industry. Several reports indicate a wave of steam cracker plants is coming up in the near future around the world, in particular, several ethane-cracker plants in the United States, to produce polyethylenes plastics of the type LDPE/LLDPE, mostly for export. Refineries are also looking for alternate technologies to remain competitive. In order to increase their profitability, one technology that is getting a lot of interest is direct conversion of crude to petrochemicals.

Some refinery technologies such as fluid catalytic cracking (FCC), delayed coking, or catalytic reforming allow the refiners the flexibility to operate to increase the production of olefins for the petrochemicals industry. Nevertheless, this requires higher severity and hence higher operating cost. Despite the higher cost, the alternate option may be profitable as the demand for petrochemicals increases. Some of the refinery technologies are discussed below.

6.4.2.1 HS-FCC process by Axens

In some cases, of course, based on economics, some refineries produce propylene as a byproduct of an FCC plant. The main purpose of an FCC plant in a refinery is to produce gasoline from heavy gas oil feedstock. So it is a challenge for the refinery to tweak the operating conditions in favor of propylene instead of gasoline, and then redirect the output line to a "propylene splitter" to produce polymer-grade propylene for the petrochemical industry. However, in the US, with increasing demand for gasoline and an increase in cheap lower hydrocarbons with the production of tight gas, C_2 / C_3 steam crackers are in greater use for the production of olefins. In some parts of the world where gasoline demand is high, they cannot afford to switch the production from gasoline to olefins. In a typical FCC plant, gaseous hydrocarbon (< C4) production could be 15 to 20 wt% of the feed, and the ethylene plus propylene production could exceed 30% of the gaseous components.

According to the Axens company website (look for the English version), due to the increasing demand for petrochemicals in Europe and the corresponding lesser availability of feedstocks at reasonable cost, they have improved the existing FCC process to maximize olefin production from the same FCC feed VGO (vacuum gas oil). The process is known as "High Severity FCC or HS-FCC ™," where they have increased the severity of the reaction conditions. Some of the selective results taken from the Axens website are shown in Table 6.4.2.1. The results clearly agree with the discussion in earlier chapters, where it says that the dehydrogenation of paraffin for olefin production increases at higher temperatures though at a higher cost. Figure 6.4.2.1 represents a simplified version of the process, redrawn from the flow diagram shown on their website.

Table 6.4.2.1 shows typical average results generated by Axens in their HS-FCC plant and comparison data with a conventional FCC plant. In the HS-FCC process, by simply increasing the reactor temperature by 100 °C, the ethylene production increased from 1.5% to 2.5% and the propylene production tripled from 5% to 16%, at the cost of a decrease in gasoline production by about 15%. By improving the catalyst performance with the increase in VGO conversion, Axens claims to achieve almost 20% propylene yield. Axens not only concentrates on the production of polymer-grade ethylene and propylene, but also on the aromatic petrochemicals as a byproduct.

Table 6.4.2.1. Average yield (wt%) of major olefins from HS-FCC as compared to the conventional FCC

	FCC (conventional)	HS-FCC
Temp, °C	500	600
Ethylene	1.5%	2.5%
Propylene	5.0%	16.0%
Gasoline	51.5%	38.0%
Coke	4.5%	6.5%

Figure 6.4.2.1 shows that they have an additional ethane steam cracker in the front of the HS-FCC plant for additional production of ethylene. This clearly suggests that there is so much demand for ethylene in Europe that it is considered as a high-performance product such that they can afford to run integrated HS-FCC and steam cracker plants.

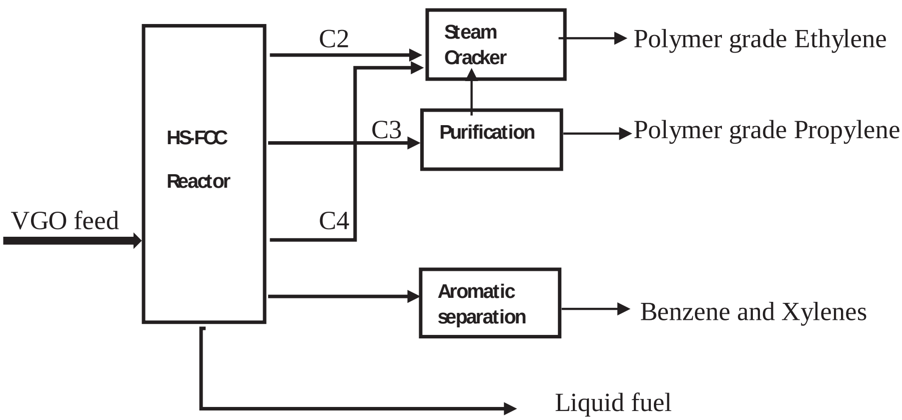

Fig. 6.4.2.1. Redrawn simplified schematic diagram of Axens HS-FCC plant

6.4.2.2 Petro-FCC™ process by UOP

In order to meet the world demand, UOP has also introduced a new option with the modification of their existing FCC process called Petro-FCC™ (Fig 6.4.2.2). In this case, the conventional FCC mode for the production of gasoline is modified to maximize the propylene yield with the introduction of several improved steps: catalyst type, reactor, regenerator, and olefin separation sections. According to the UOP website, propylene yield increases to about 20%. They also claim to have the capability to control the propylene yield based on market demand.