PETROCHEMICALS

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Contents

Summary

This chapter covers the petrochemicals that make up the majority of the volume of the thousands of different products and that make up the petrochemicals industry. For each product, the processes, the commercial aspects including logistics and application are covered.

1. Introduction

The Petrochemical industry covers hundreds of products, scores of processes and thousands of manufacturing complexes, almost every one with multiple process facilities. Together they produce billions of pounds of products. All that is responding to consumers who find petrochemicals finished products all around them – in their clothing, furnishings, consumables, entertainment devices, transportation vehicles, and in many other categories.

Activities involving the creation of petrochemicals can be considered to have been started in 1828 when chemist Friedrich Wöhler discovered that organic materials (compounds made up of carbon and hydrogen atoms) could be synthesized from inorganic chemicals. Significant commercial activity didn't start until the next century and, like most innovations, grew slowly for several decades.

The advent of plastics in the 1930s started serious substitution of petrochemicals for traditional materials that accelerated through most of the 20th century. In the process, petrochemical products, especially polymers, took markets away from diverse categories, as in the following examples:

- fibers, especially wool and cotton by polyesters, nylon, and polypropylene
- glass, by plastic bottles and window materials
- wood, by plastic facades and glued structural materials
- coatings, by latex paints
- metals by structural and flexible plastics

Not all petrochemicals end up as plastics. For example, methanol is used to make fuels; ethyl alcohol is used as a pharmaceutical; ethylene glycol is an aircraft de-icer and automotive coolant.

1.1. Industry Structure

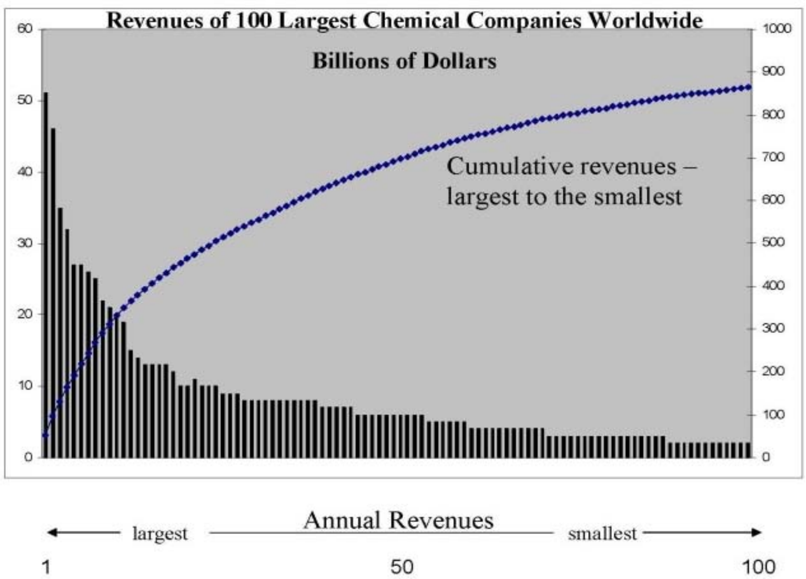

Figure1. Petrochemicals industry structure

Because of its breadth of products, thousands of companies compete in the industry. While some of the firms are huge, international enterprises, the ten largest international companies account for about $3000 billion in revenues. The next 90 largest have another $550 billion (Fig. 1). Beyond that, the thousands of smaller firms add an even larger amount.

As in may other industrial activities, mergers, acquisitions, and new entries in the petrochemicals industry have been continuous from the beginning. Nearly half the petrochemical volumes come from different companies that produced them three decades ago.

1.2. Manufacturing Facilities

Petrochemicals have their origins in the extractive industry – oil, natural gas and coal. Petroleum, of course, donated its name to petrochemicals. Oil refineries were the early producers of the base chemicals from which most finished products ultimately are derived. The natural gas processing industry also provides feedstocks, ethane, propane, and butanes to petrochemical processes that make the base petrochemicals. Curiously enough, steel mills provide a modicum of base petrochemicals as a by-product of their coal-to-coke process.

But today, most petrochemical plants are located in proximity to oil refineries or natural gas plants because that's where the molecules are.

1.3. The Chemistry of Petrochemicals

Understanding petrochemicals calls for some appreciation of the chemical principles behind them and the chemical structures of the products. The following gives a simplified discourse to accomplish that.

Three reasons account for such diverse petrochemical products. All of them have to do with the carbon atom, which together with the hydrogen atom, are present in all petrochemicals.

- carbon is an abundant, readily available substance found in oil, natural gas and coal
- the carbon atom has a propensity to attach itself to four other atoms, including other carbon atoms. That gives carbon a valence of four. Other atoms have different valences – hydrogen has a valence of one, oxygen two, chlorine one, etc. (Attach in this context means an electrical attraction that keeps the atoms together. Illustrations in this chapter will show these attachments as straight line or dashes.)
- When several or more carbon atoms are involved, they can be attached in different configurations (connected differently with each other and with other atoms) and still satisfy the valence (connections) requirements of four. When they do, even though the molecules have the same number of atoms, they behave differently – chemically and physically. They are different petrochemicals, even though they have the same chemical formula.

The simplest organic chemical compounds are methane, ethane, and propane as shown below.

```
                 H
                 |
Methane:   H  –  C  –  H                 or  CH4
                 |
                 H
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```
              H     H
              |     |
Ethane:  H –  C  –  C  –  H              or  C2H6
              |     |
              H     H
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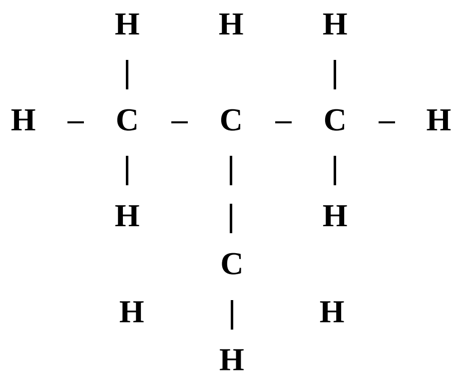
               H     H     H
               |     |     |
Propane:  H –  C  –  C  –  C  –  H    or  C3H8
               |     |     |
               H     H     H
```

In each case the valence of the carbon atoms and the hydrogen atoms are satisfied. Beyond these simple organic compounds, different structures called isomers are possible, as with normal butane and isobutane as shown below.

```
                        H     H     H     H
                        |     |     |     |
Normal butane:     H –  C  –  C  –  C  –  C  –  H
                        |     |     |     |
                        H     H     H     H
```

These chemicals have the same chemicals formula, C_4H_{10}, but the structure of the two molecules differs. That gives rise to different properties – gravity, volatility, ease of reacting with other chemicals, and more. As the number of carbon atoms in an organic compound increases, and there can be scores of them, the number of different isomers increases exponentially. For that reason, and because there are other types of atoms that carbon can connect to, there are nearly a million different organic compounds that have been identified. Only a handful of them can be covered in this chapter.

Isobutane :



Petrochemicals can be categorized in many ways, but a simple list includes:

- paraffins, such as methane, propane butane, isobutane, hexane
- olefins, such as ethylene, propylene, butylene, isobutylene
- cyclics, including aromatics such as benzene, toluene and xylenes
- oxygen-containing, such as ethyl alcohol, propylene oxide
- nitrogen-containing, such as amines
- oligomers, such as alpha olefins
- polymers, such as polyethylene, nylon, polyester, epoxies

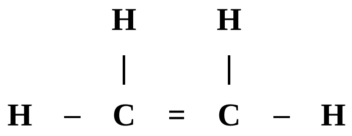
Even this simple list insufficiently describes petrochemicals because some of the polymers have oxygen or nitrogen, as do some of the cyclics. In this discussion, the structures of each category are described in more detail as they are encountered in the discussion of the individual petrochemicals.

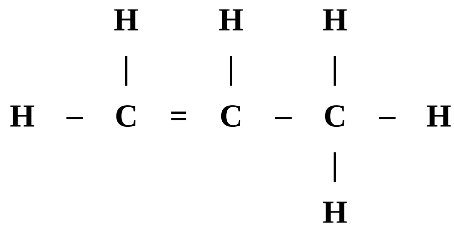
2. Base Chemicals

Most petrochemicals start from just a handful of base chemicals: ethylene, propylene, butylenes, benzene, toluene, xylenes, and synthesis gas. To confound the discussion, several of these seven come from two or three different processes. That makes it easier to start with an olefins *plant* rather than with the olefins, because all but synthesis gas come from olefins plants.

2.1. Olefins plants

The ethylene and propylene molecules in shown in the following resemble ethane and propane shown earlier. However they have double bonds between two of the carbon atoms. That accommodates the facts that two hydrogen atoms are missing from each. In order to satisfy the valence, the propensity for carbon atoms to attach to four other atoms, two carbons have two bonds connecting them, a complex arrangement of electron sharing between the two. While it may appear graphically that the double bond is twice as strong as the single bond, the reverse is true. Double bonds imply an unsatisfying condition, one that makes the double bonded carbon atom susceptible to chemical reaction with another atom or molecule to form a new compound that satisfies the valence of four with a single bond. For that reason, ethylene and propylene are the starting feedstocks for more than half the petrochemicals.

Ethylene :  or $\mathbf{CH_2 = CH_2}$

Propylene :  or $\mathbf{CH_2 = CH - CH_3}$

The original petrochemical plants that produced ethylene and propylene made them from the most obvious raw materials, ethane and propane. These two hydrocarbons are recovered both from natural gas and in petroleum refining.

In an olefin plant that uses ethane and/or propane as feed, high temperatures cause the ethane and propane to crack, splitting them into two or more new molecules. In the case of ethane, the feed passes through a reactor heated to 800-900^{o}C in less than a second. Typically about 60% of the ethane cracks, about 80% of that to ethylene, the rest into other by-products. By recycling the 40% that did not crack, the yield of ethylene increases to about 80%. See Table 1.

	Ethane	**Propane**	**Butane**	**Naphtha**	**Gas Oil**
Ethylene	0.80	0.40	0.36	0.23	0.18
Propane/ Propylene	0.03	0.08	0.20	0.13	0.14
Butane/ Butylene	0.02	0.02	0.05	0.15	0.06
Butadiene	0.01	0.01	0.03	0.04	0.04
Fuel Gas	0.13	0.38	0.30	0.26	0.18
Pygas	0.01	0.01	0.06	0.18	0.18
Gas Oil				0.01	0.12
Pitch					0.10

Table 1. Olefin plant yields

Downstream of the cracking furnaces are various vessels and equipment to separate the several compounds that come out. Since most of them have very low boiling temperatures, both refrigeration and distillation columns are used to separate out an ethylene stream of 99+% purity.

When feedstocks heavier than ethane, that is, propane, butane, naphtha, and gas oil, are used as feed to an olefin plant, several things change:

- the yield of ethylene is lower (Table 1)
- the yield of propylene is higher

- the furnaces that that heat up the feed have to be correspondingly higher to produce the same amount of ethylene
- the separation equipment downstream of the cracking section has to be more elaborate because so much more co-product is produced.

2.1.1. Olefin Plant Co-product

The co-product gases produced in olefin plants are shown in Table 1. The methane and hydrogen are typically used as fuel in the plant fuel system. The butane/butylene and butadiene streams are covered in more detail in Section 4.0. The produced streams that are heavier than the butane/butylenes are generally sold into the refining industry.

The gasoline/naphtha, sometimes call pyrolysis gasoline or pygas, is used as a gasoline blending component. This stream can be rich in aromatics and can be processed to remove the benzene, toluene, and xylenes, as covered in Section 3.0. The gas oil and pitch streams are generally used to make industrial fuel oils.

All these streams have high olefin content. That is, many of the molecules in them have double-bonded carbons. This is a result of the cracking process, where there is an insufficient amount of hydrogen to fill out the carbon atom valence of four.

The reactivity of the double-bonded olefins makes them susceptible to reactions that form gummy material and other undesirable compounds during combustion and even if these streams are left in storage for a while.

These streams tend to be rich in aromatic compounds, not only the benzene, toluene, and xylenes, but also larger molecules having a benzene ring in them. The benzene ring has a resilient structure so that cracking is less likely to break the ring apart, even if it is part of a large complicated molecule.

Like olefins, aromatic compounds tend to make for poor quality fuel oil use. These olefin plant streams typically have to be separately treated with hydrogen to make the quality suitable for marketing.

2.2. Ethylene

Ethylene, C_2H_4, is the simplest of the olefins family of petrochemicals. The double bond in it makes it reactive – susceptible to combining with other molecules, including other ethylene molecules.

One of the three most used base chemicals beside propylene and benzene; ethylene is the starting point for polyethylene, acetic acid, styrene, ethylene oxide, and many more multi-billion pound derivatives. More than 60% eventually ends up as a polymer of some kind.

In the olefins plant, ethylene is purified to 99.5% or higher. The stream is treated to remove any acetylene content, an anathema to ethylene users.

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Biographical Sketches

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1961 BS – Industrial Management, M.I.T.
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1999-2002 Lecturer at Southern Methodist University
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Oil & Gas Pipelines in Nontechnical Language (PennWell 2006)
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Deepwater Exploration & Production – a Nontechnical Guide (PennWell 2003)
Petroleum refining for the Non-technical Person (PennWell 3rd edition 1999)
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