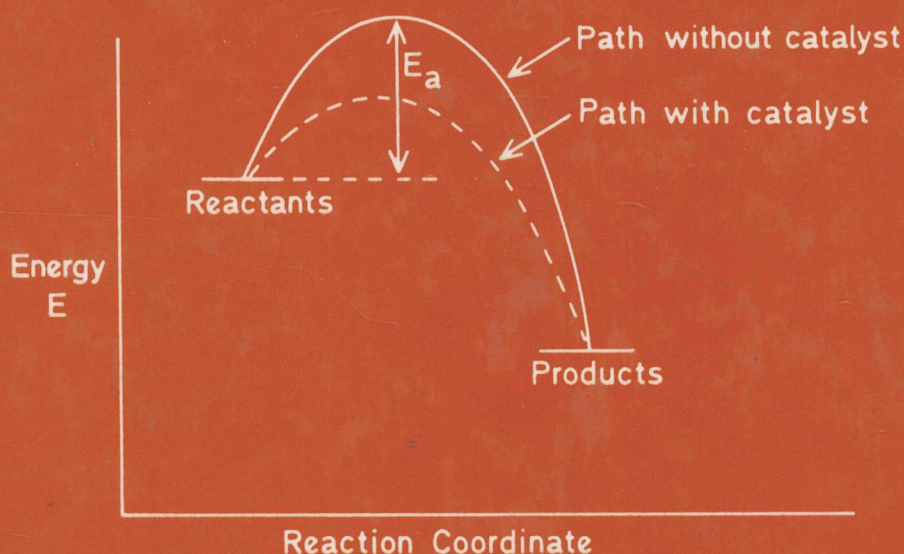


Catalysis in Petrochemical Processes

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KLUWER ACADEMIC PUBLISHERS

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CATALYSIS IN PETROCHEMICAL PROCESSES

Preface

The field of petrochemicals started some years ago with the simple addition reaction of water to propylene for the production of isopropyl alcohol. Currently, the petrochemical industry has become a multi-billion dollar enterprise which encompasses a wide field of chemical products. Almost all the basic organic reactions such as hydrogenation, alkylation, substitution, polymerization, etc. are utilized for the production of these chemicals. It may not, however, have been possible to establish this huge industry without the use of different catalysts. In other words, the great advancements in the catalytic area have supported the vast developments in the petrochemical field.

In this book, we have adopted the idea of discussing the petrochemical industry from the point of view of reactants' activities and susceptibilities toward different catalysts. The book is thus classified according to the reaction type. This will enable students and other users of the book to base their understanding of the petrochemical field on the fundamental principles learned in chemistry. However, the first chapter is aimed at establishing some basic facts on the petrochemical industry and its major uses. It discusses, without going into details, the raw materials used, the intermediates and the downstream products. The next eight chapters discuss in some detail the main reactions and the catalysts used for the production of chemicals and polymers from petroleum. The last chapter is devoted to a discussion of some of the practical techniques used in the catalytic field.

The book is considered to be an important supplement to the background of students studying industrial chemistry, chemical engineering, and to technical staff working in the petroleum and the petrochemical field. However, the book is intended to be used as a research monograph. The authors felt that a full literature review of the subjects discussed is not necessary. Only selected up-to-date references, which have either been used in compiling the background for the text, or are recommended for supplementary reading, are presented at the end of each chapter. Instructors in the fields of chemistry, chemical engineering and industrial chemistry will find this book a feasible core for a senior undergraduate or a graduate course in applied chemistry.

We, the authors, hope that the state of the art, as it is now, has been well-summarized, fulfilling the objective of publishing this book.

SAMI MATAR
MANFRED MIRBACH
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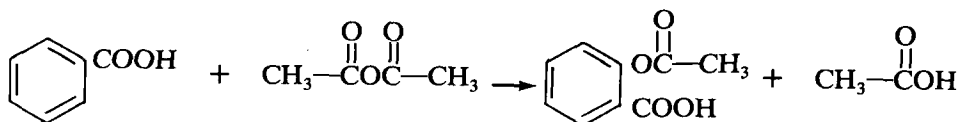
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Raw Materials and Chemicals from Carbonaceous Sources

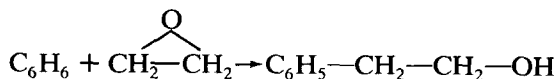
1. Introduction

Petrochemicals, or petroleum chemicals, are organic compounds derived from natural gas, associated gas or crude oils. These do not include organic compounds produced from other natural sources, whether from animal or plant origin such as fats, oils, cellulose etc.

However, petrochemicals may also be derived from such other carbonaceous materials as coal, peat, tar sands and oil shale. Examples of downstream polymers and chemicals from petroleum and other carbonaceous sources include synthetic fibers, plastic rubber, nitrogen fertilizers such as urea, solvents such as ethylene glycol, surface active agents such as synthetic detergents and many others. The petrochemical field is a very diversified one, and several intermediates and chemicals from petroleum are used in specialized organic industries such as pharmaceuticals, pesticides, explosives, fragrances etc. For example, aspirin (acetylsalicylic acid) is produced by reacting salicylic acid and acetic anhydride.



Salicylic acid is produced from phenol and carbon dioxide. Acetic anhydride is produced from methanol and carbon dioxide. All these chemicals are either products or by-products of the petroleum and petrochemical industries. Another example, which illustrates the relation between the petrochemical field and the perfumery field, is the synthesis of phenylethyl alcohol, which has the smell of orange flowers. This alcohol can be prepared by reacting phenyl magnesium bromide (Grignard reagent) with ethylene oxide. It can also be produced by a direct alkylation of benzene with ethylene oxide.



Both benzene and ethylene oxide are important petrochemical intermediates for preparing a substantial number of compounds.

1.1. Raw Materials

As mentioned before, the raw materials used for producing intermediates for the

petrochemical industries are natural gas, associated gas, and crude oils. Other carbonaceous materials could also be utilized for the same purpose.

1.1.1. NATURAL AND ASSOCIATED GASES

Natural gas is a term used for a gas mixture found in porous underground reservoirs. If the gas is dissolved under pressure with crude oils, it is called associated gas. Both natural and associated gas are composed of a mixture of light hydrocarbons plus other non-hydrocarbon gases. Depending on the topographical history of each reservoir, the ratio of the gas constituents may differ greatly from one gas reservoir to another. The main constituent of these gases, however, is methane. A major difference between natural and associated gas is the ethane/methane ratio which is usually much higher in associated gas than in natural gas. Table 1-1 shows a typical analysis of some selected natural and associated gases. As can be seen, natural gas may contain a high percentage of other non-hydrocarbon gases such as carbon dioxide, hydrogen sulfide, nitrogen and helium. Both hydrogen sulfide and carbon dioxide are acidic gases which should be eliminated or reduced to non-harmful levels before utilizing the gas. Natural gas is mainly used as a fuel. However, many petrochemical industries are based on natural and associated gas. For example, Saudi Arabian petrochemical plants at Jubail and Yanbu are mainly based on associated gas as a petrochemical feedstock as well as a fuel. Methane, the major component of natural and associated gas, is the simplest hydrocarbon. As a chemical compound it is utilized for the production of synthesis gas. Synthesis gas is the precursor of many important chemicals.

Natural Gas Treatment

Before utilizing natural gas as a fuel or as a petrochemical raw material, it has to be treated to remove or reduce the amount of acid gases, adjust the humidity and free the gas from heavier hydrocarbon components.

Table 1-1. Typical analysis of selected natural and associated gases.

Component	Natural Gases			Associated Gases		
	Salt Lake U.S.	Klifside U.S.	Larcq France	Libya	Saudi Arabia Abqaiq	North Sea U.K.
Methane	95.0	65.8	70.0	66.8	62.24	85.9
Ethane	0.8	3.8	3.0	19.4	15.07	8.1
Propane	0.2	1.7	1.4	9.1	6.64	2.7
Butane	...	0.8	0.6	3.5	2.40	0.9
Pentanes & heavier	...	0.5	...	1.2	1.12	0.3
Hydrogen sulfide	15.0	...	2.80	...
Carbon dioxide	3.6	0.6	10.0	...	9.20	1.6
Nitrogen	0.4	25.6	0.5
Helium	...	1.8

Hydrogen Sulfide and Carbon Dioxide Removal

Treatment of acid gases found in natural or associated gases can be effected either by a chemical absorption scheme or by the use of physical absorbents. In the first scheme, natural gas is passed through an easily regenerated base such as diethanolamine. The solvent used, which contains carbonates and sulfides, is then regenerated by steam treatment. Other amines are also used for the same purpose such as monoethanolamine and diglycolamine. The aqueous solution of the latter has a lower freezing point than the other amines which makes it usable under colder conditions. It also has a high treatment capacity at elevated temperatures.

Physical absorbents are compounds which have the ability to dissolve the acid gases without forming chemical bonds with them. Physical absorbents are more commonly used when the gas contains a high percentage of carbon dioxide. In the Selexol process, for example, the physical solvent is the dimethylether of polyethylene glycol ($\text{CH}_3\text{—}[\text{OCH}_2\text{CH}_2]_n\text{—OCH}_3$).

These solvents are more active at higher pressures and they are therefore suitable for treating compressed natural gas. Solid adsorbents are also used for the treatment of acid gases. Molecular sieves (aluminosilicate compounds) are solid compounds of this type which may also be utilized for adjusting the gas humidity by adsorbing water.

Humidity Treatment

Natural and associated gases have to be dehydrated to prevent hydrate formation during the transfer of the gas by pipeline. Hydrates are solid compounds formed by a physico-chemical reaction between the hydrocarbon gases and water under high pressures.

Treatment starts by passing the gas under normal pressure through a polar solvent which dissolves water but not the hydrocarbon gases. Solvents used for this purpose should have a low vapor pressure, such as ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG). The last solvent is preferred in vapor-phase processes because of its low vapor pressure which results in low glycol losses. Molecular sieves, as mentioned above, could be used for the dual purpose of reducing the humidity as well as removing the acid gases from natural and associated gases.

Heavy Hydrocarbons Removal

After treating the gas as described above, it is now dry and sweet. A further step has to be undergone before using the gas, and that is the removal of gases heavier than methane by a cooling scheme. Liquid propane is used to cool natural gas. The cold gas is then washed with a hydrocarbon liquid which dissolves the condensable hydrocarbons. Methane mixed with a small amount of ethane is collected for use as a fuel or as a petrochemical feedstock. Table 1-2 is a typical analysis of a treated natural gas. The condensable hydrocarbons normally known as 'Natural Gas Liquids', are separated from the hydrocarbon solvent and then fractionated.

Table 1-2. Typical analysis of a treated natural gas.

Component Mole %	Before Treatment	After Treatment
C1	70.35	94.85
C2	0.83	0.99
C3	0.22	0.003
C4	0.13	0.004
C5 ⁺	0.17	0.018
N ₂	0.45	0.62
CO ₂	27.85	3.50
H ₂ S	0.0013	—

Ethane may be separated from the upper fractionation zone and used as a feed to an ethane cracker. Both propane and butane are usually separated together, then liquefied and used as liquefied petroleum gas (LPG). The last fraction, composed of hydrocarbons heavier than C-4, is called 'Natural Gasoline'. This fraction may contain some unseparated butanes and is customarily added to gasoline to raise its vapor pressure.

1.1.2. CRUDE OILS

A crude oil is a black viscous mixture which varies greatly in density from one oil well to another. Unlike natural gas, a crude oil is mainly composed of a heavier mixture of hydrocarbons. The principle hydrocarbon classes of the mixture are; paraffins, cycloparaffins (naphthenes) and aromatics. Olefinic compounds are essentially not present in crude oils. Depending on the origin of the crude oil and on the conditions under which it is formed, the ratio of these hydrocarbon classes varies appreciably from one crude to another. In addition to the hydrocarbons, crude oils may contain appreciable amounts of sulfur, nitrogen and oxygenated hydrocarbon derivatives, along with smaller amounts of organometallic compounds. Iron, nickel and vanadium compounds are examples of organometallics which may be found in trace amounts in crude oils and their fractions. However, the presence of nickel, and vanadium compounds above certain levels in oil fractions and fuel oils is poisonous to many catalysts used in petroleum and petrochemical processes. Table 1-3 shows a typical analysis of some representative crude oils.

Crude oils, are generally classified into three types depending on the ratio of the hydrocarbon class that predominates in the mixture. These are:

- a — Paraffinic: — constituents are predominantly paraffinic hydrocarbons. Low percentage of aromatics and asphaltenes.
- b — Naphthenic: — contain relatively a higher ratio of cycloparaffins, and a higher amount of asphalt than in paraffinic crudes.

Table 1-3. Typical analysis of some representative crude oils.

Tests	Jalo (Libya)	Alamein (Egypt)	Amer (Egypt)
Specific Gravity @ 60/60°F		0.8576	0.9255
Gravity API @ 60°F	33.8	33.41	21.39
Water Content vol %	0.05	0.2	0.1
Salt Content wt %	0.003	0.007	0.005
Total Sulfur wt %	0.68	0.86	4.5
Hydrogen Sulfide, ppm	—	—	6311
Mercaptan Sulfur, ppm	—	—	86
Pour Point, °F	9	35	30
Conradson Carbon Residue wt %	1.4	4.9	4.5
Ash Content, wt %	0.0012	0.004	0.05
Asphaltene Content wt %	0.25	3.37	8.06
Paraffin Wax Content wt %	4.0	3.3	1.35
Vanadium Content, ppm	9	15	67
Phenol Content, wt %	—	—	0.0082

c — Asphaltic: — contain a relatively large amount of fused aromatic rings and a high percentage of asphalt.

However, there is no sharp borderline separating these three classes. In general, paraffinic crudes are less dense and are easier to process than the other two classes.

The specific gravity (or API) is an important parameter which is sometimes used to indicate the crude-oil quality. A low density crude (high API) has a higher percentage of the more valuable light and middle distillates. Oils with a high sulfur content are less in demand than those with a low sulfur content since fractions from the former oils have to be subjected to further treatment to remove these sulfur compounds (see Chapter 3, 'Hydrodesulfurization').

In processing crude oils, naphtha is obtained from the upper fractionator zone. Naphtha is composed of a light hydrocarbon mixture approximately in the range of C-5—C-11.

Naphtha obtained from a highly naphthenic crude is easier to catalytically reform to a high octane gasoline than naphtha from a paraffinic crude, since the rate of aromatization of naphthenes is faster than that of paraffins. Catalytic reforming is a process used to change cycloparaffins and paraffins in the naphtha range to aromatics (see Chapter 3, 'Dehydrogenation'). It is a major process for producing benzene, toluene and xylenes (BTX). These compounds are precursors to many other chemicals. Middle fractions obtained from distilling crude oils are kerosine and gas oil. Fuel oil is taken from the lower zone of the fractionator. These fractions are mainly used as fuels for different purposes. However, gas oils and fuel oils may be further catalytically cracked to produce more gasoline and kerosine. The gasoline obtained from catalytic crackers is highly aromatic and may

also be used to separate BTX compounds for petrochemical use. Kerosine is mainly used as a jet fuel. However, *n*-paraffins for detergent production may be separated from kerosines.

1.1.3. COAL, PEAT, OIL SHALE AND TAR SANDS

Coal, peat, oil shale and tar sands are materials which are mainly constituted of carbon. The H/C ratio of these materials is appreciably lower than that of most crude oils, (Table 1-4). They are classified, however, with crude oils as carbonaceous materials. Their origin may bear some similarity to that of crude oils. In a way, these substances were formed by the action of heat and pressure on some organic remains — whether of animal or plant origin — which decomposed to the final form (oil, coal, etc.). It is generally accepted, for example, that coal originated from land plant debris that decayed under mildly reducing conditions, while crude oils are formed from sea plants and animals decaying under highly reducing conditions. Peat is considered to be immature or young coal.

Coal and Peat

Coal is one of the major fossil energy sources of our time. It has been responsible for powering the industrial revolution in Europe and America for more than a century. However, since World War II, coal as a primary energy source has been overshadowed by oil, which is a cleaner, more convenient fuel to handle and process. However, coal is currently supplying about 28% of the world's energy needs.

Coal has been and still is a source of organic chemicals. For example, liquid coke-oven by-products from coal carbonization still provide about 6% of the benzene demand. If coal gasification and liquefaction become economically feasible in the future, coal could be a major source of organic chemicals.

Coals are classified into different ranks according to the degree of chemical change that has taken place due to the decay of the remains. Peat, sub-bituminous, bituminous and anthracite are different ranks of coal. The first type being the one that has been subjected to the least change, while the last has suffered the highest conversion. Anthracite is characterized by having a higher C/H ratio than other coal ranks. Table 1-4 shows the carbon, hydrogen and oxygen analysis of some coals, compared with a typical crude oil.

Table 1-4. Typical elemental analysis of some coals compared with a crude oil.

	C	H	S	N	O	H/C Ratio
Crude Oil	84.6	12.8	1.5	0.4	0.5	1.82
Peat	56.8	5.6	0.3	2.7	34.6	1.18
Lignite	68.8	4.9	0.7	1.1	24.5	0.86
Bitumenous Coal	81.8	5.6	1.5	1.4	9.7	0.82
Anthracite	91.7	3.5			2.7	0.46

The higher C/H ratio of coals in comparison to crude oils may be a manifestation of the strong reducing conditions under which crude oils have been formed. Adjustment of the C/H ratio of coals, in order to be comparable to that of crude oils, may be done through liquefaction or catalytic hydro-liquefaction processes. Products from these conversion processes are called synthetic crude oils, which may further be treated to produce conventional fuels and chemicals.

Oil Shale

Oil shale is a naturally low permeability rock made of an inorganic mineral matter which is interspersed with a high molecular-weight organic waxy substance called 'kerogen'. This waxy substance is not very soluble in organic solvents. When shale is heated, kerogen decomposes to a liquid-shale oil that can be processed to products similar to petroleum fractions. The oil yield ranges between 10–20 wt % of the total shale.

Oil shale composition may differ substantially from one shale to another. Table 1-5 shows the analysis of two shale deposits (Eastern and Western) in U.S. The 'Fischer assay', is a test that indicates the amount of kerogen that can be obtained from the shale.

To separate kerogen from the inorganic matter, shale is subjected to a retorting process in which crushed shale is heated to high temperatures to pyrolyze the high molecular weight organic polymer. Oil produced by retorting shales is a thick viscous material which is sometimes called synthetic crude oil.

The H/C ratio (approximately 1.6) of this oil is somewhat lower than that of most crude oils. However, its composition is quite different. The nitrogen and the oxygen contents are usually higher but the sulfur content is much lower than that of crude oils. Attempts to utilize the organic matter of the huge shale deposits through retorting followed by hydrotreatment have been successful. However, an obstacle that hinders the progress in this line, is the disposal of the massive solids from retorting processes.

Table 1-5. Typical analysis of U.S. eastern and western shales.

	Eastern	Western
Ultimate Analysis, wt % (dry basis)		
Organic Carbon	13.7	13.6
Hydrogen	1.64	2.1
Sulfur	4.72	0.5
Carbon Dioxide	0.5	15.9
Ash	78.3	66.8
Fisher Assay Analysis		
Oil Yield, wt %	4.6	11.4
Water Yield, wt %	2.3	1.6
Loss + Gas, wt %	2.4	2.6
Assay, gal/ton	10.3	29.8

Tar Sands

Tar sands, also called oil sands or bituminous sands, are mainly composed of sand saturated with bitumen and water. Tar sand deposits are found in large accumulations in a few parts of the world. About 98% of all tar sand is found in seven deposits, the largest of which are the Athabasca deposits in Western Canada. These deposits are covered by a semifloating mass of partially decayed vegetation approximately 6 meters thick.

The bitumen, a heavy viscous mixture, is mainly constituted of heavy hydrocarbon compounds. Recovering the bitumen differs from getting crudes from oil wells. Oil sands are either strip mined, if the deposits are near the surface, or recovered *in situ* if they are in deeper beds. Bitumen is then extracted by hot water. The bitumen changes to a fluid when heated and floats on the water surface. Cooling changes it to a semi-solid, viscous, dense material which is heavier than water. Table 1-6 shows a typical analysis of recovered bitumen from Athabasca-deposits. The H/C ratio of tar sands bitumen is intermediate between those of coals and crude oils. Complex polynuclear aromatics are the major components of these bitumens. However, the quality of products obtained by distilling the bitumen could be improved greatly by hydroprocessing schemes.

1.2. Intermediates for Petrochemical Production

Intermediates used for producing different petrochemicals are simple reactive compounds such as olefins, diolefins, alcohols, aldehydes, aromatics etc. These

Table 1-6. Typical analysis of Athabasca bitumen.

API Gravity	6.0
Pour Point °F	11.2
Calorific Value Btu/lb	17,900
<i>Components wt %</i>	
Asphaltenes	20.0
Resins	25.0
Oils	55.0
<i>Ultimate Analysis</i>	
Carbon	83.6
Hydrogen	10.3
Sulfur	5.5
Nitrogen	0.4
Oxygen	0.2
H/C Atom Ratio	1.5
<i>Heavy Metals ppm</i>	
Nickel	100
Vanadium	250
Copper	5