Lecture 1: Petrochemicals: Overview

1.1 Introduction

- In this lecture, we present a brief overview of petrochemical technologies and discuss upon the general topology of the petrochemical process technologies.

- Petrochemicals refers to all those compounds that can be derived from the petroleum refinery products

- Typical feed stocks to petrochemical processes include

- C1 Compounds: Methane & Synthesis gas
- C2 Compounds: Ethylene and Acetylene
- C3 Compounds: Propylene
- C4 Compounds: Butanes and Butenes
- Aromatic Compounds: Benzene

- It can be seen that petrochemicals are produced from simple compounds such as methane, ethylene and acetylene but not multicomponent products such as naphtha, gas oil etc.

- 1.1.1 Definition: These are the chemicals that are made from petroleum and natural gas. Petroleum and natural gas are made up of hydrocarbon molecules, which comprises of one or more carbon atoms, to which hydrogen atoms are attached.

- About 5 % of the oil and gas consumed each year is needed to make all the petrochemical products. Petrochemicals play an important role on our food, clothing, shelter and leisure. Because of low cost and easy availability, oil and natural gas are considered to be the main sources of raw materials for most petrochemicals.

1.1.2 Classification: Petrochemicals can be broadly classified into three categories:-

a. Light Petrochemicals: These are mainly used as bottled fuel and raw materials for other organic chemicals. The lightest of these -- methane, ethane and ethylene -- are gaseous at room temperature. The next lightest fractions comprise petroleum ether and light naphtha with boiling points between 80 and 190 degrees Fahrenheit.

b. Medium Petrochemicals: Hydrocarbons with 6 – 12 carbon atoms are called "gasoline", which are mainly used as automobile fuels. Octane, with eight carbons, is a particularly good automobile fuel, and is considered to be of high quality. Kerosene contains 12 to 15 carbons and is used in aviation fuels, and also as solvents for heating and lighting.

c. Heavy Petrochemicals: These can be generally categorized as diesel oil, heating oil and lubricating oil for engines and machinery. They contain around 15 and 18 carbon atoms with boiling points between 570 and 750 degrees Fahrenheit. The heaviest fractions of all are called "bitumens" and are used to surface roads or for waterproofing.

Bitumens can also be broken down into lighter hydrocarbons using a process called "cracking."

1.2 Process Topology

- ***Reactors:*** Reactors are the most important units in petrochemical processes. Petrochemicals are manufactured by following simple reactions using relatively purer feed stocks. Therefore, reaction chemistry for petrochemicals manufacture is very well established from significant amount of research in this field. Essentially all petrochemical processes need to heavily depend upon chemical transformation to first product the purification.

- Separation: With distillation being the most important unit operation to separate the unreacted feed and generated petrochemical product, the separation processes also play a major role in the process flow sheet. Where multiple series parallel reactions are involved, the separation process assumes a distillation sequence to separate all products from the feed. A characteristic feed recycle will be also existent in the process topology. Apart from this, other separation technologies used in petrochemical processing units include phase separators, gravity settling units and absorption columns. Therefore, the underlying physical principle behind all these separation technologies is well exploited to achieve the desired separation.

- Dependence on Reaction pathway: A petrochemical can be produced in several ways from the same feed stock. This is based on the research conducted in the process chemistry. For instance, phenol can be produced using the following pathways

- Peroxidation of Cumene followed by hydrolysis of the peroxide
- Two stage oxidation of Toluene
- Chlorination of Benzene and hydrolysis of chloro-benzene
- Direct oxidation of Benzene

- We can observe that in the above reaction schemes, there are two reaction pathways for phenol from benzene i.e., either chlorination of benzene or oxidation of benzene. Therefore, choosing the most appropriate technology for production is a trivial task.

- Complexity in pathway: In the above Cumene example case, it is interesting to note that toluene hydrodealkylation produces benzene which can be used to produce phenol. Therefore, fundamentally toluene is required for the generation of various petrochemicals such as benzene and phenol. In other words, there is no hard and fast rule to say that a petrochemical is manufactured using a suggested route or a suggested intermediate petrochemical. Intermediate petrochemicals play a greater role in consolidating the manufacture of other downstream petrochemicals.

Petrochemical plant in the Kingdom of Saudi Arabia

Petrochemicals (also known as **petroleum distillates**) are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels, such as coal or natural gas, or renewable sources such as corn, palm fruit or sugar cane.

The two most common petrochemical classes are:-

1- Olefins (including ethylene and propylene) and
2- Aromatics (including benzene, toluene and xylene isomers).

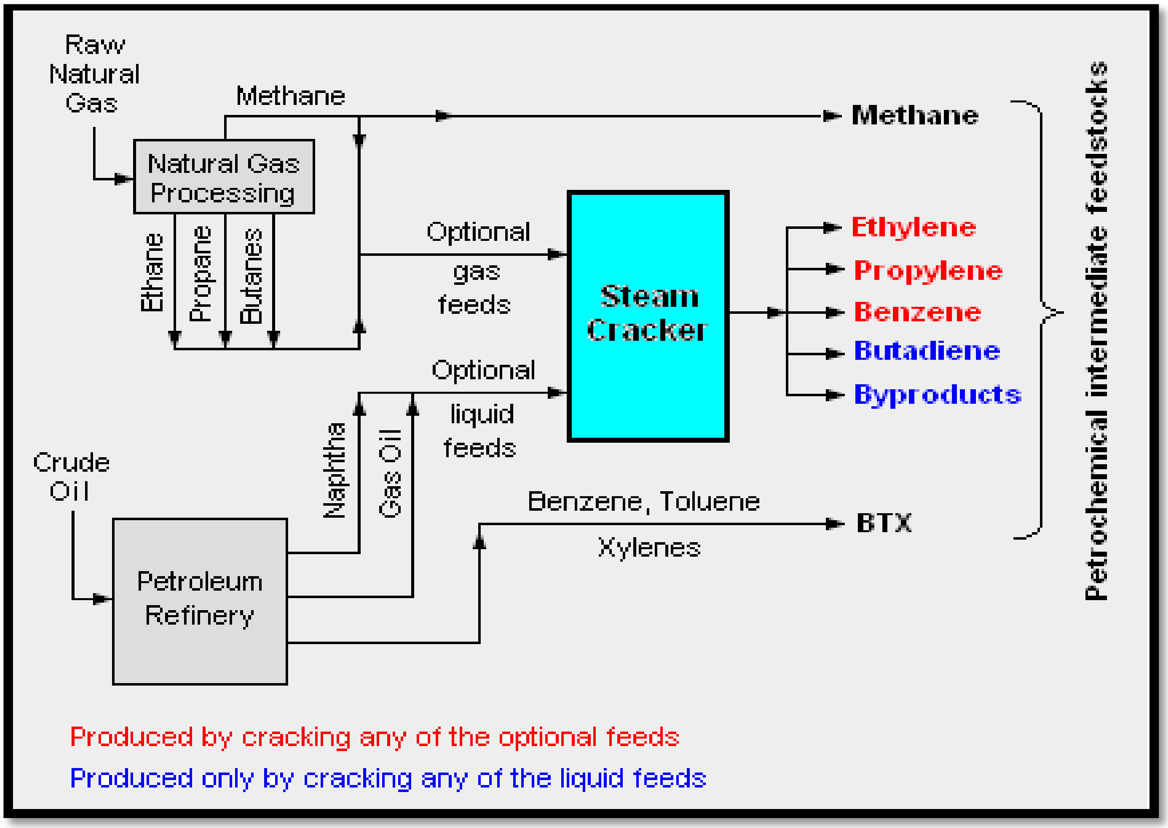
Oil refineries produce olefins and aromatics by fluid catalytic cracking of petroleum fractions. Chemical plants produce olefins by steam cracking of natural gas liquids like ethane and propane. Aromatics are produced by catalytic reforming of naphtha.

Olefins and aromatics are the building-blocks for a wide range of materials such as solvents, detergents, and adhesives. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, and gels.[1][2]

Global ethylene and propylene production are about 115 million tonnes and 70 million tonnes per annum, respectively. Aromatics production is approximately 70 million tonnes. The largest petrochemical industries are located in the USA and Western Europe; however, major growth in new production capacity is in the Middle East and Asia. There is substantial inter-regional petrochemical trade.

Primary petrochemicals are divided into three groups depending on their chemical structure:

- Olefins includes Ethene, Propene, Butenes and butadiene. Ethylene and propylene are important sources of industrial chemicals and plastics products. Butadiene is used in making synthetic rubber.
- Aromatics includes Benzene, toluene and xylenes, as a whole referred to as BTX and primarily obtained from petroleum refineries by extraction from the reformate produced in catalytic reformers using Naphtha obtained from petroleum refineries. Benzene is a raw material for dyes and synthetic detergents, and benzene and toluene for isocyanates MDI and TDI used in making polyurethanes. Manufacturers use xylenes to produce plastics and synthetic fibers.
- Synthesis gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol. Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate. Steam crackers are not to be confused with steam reforming plants used to produce hydrogen and ammonia.



Primary Raw Materials for Petrochemicals:-

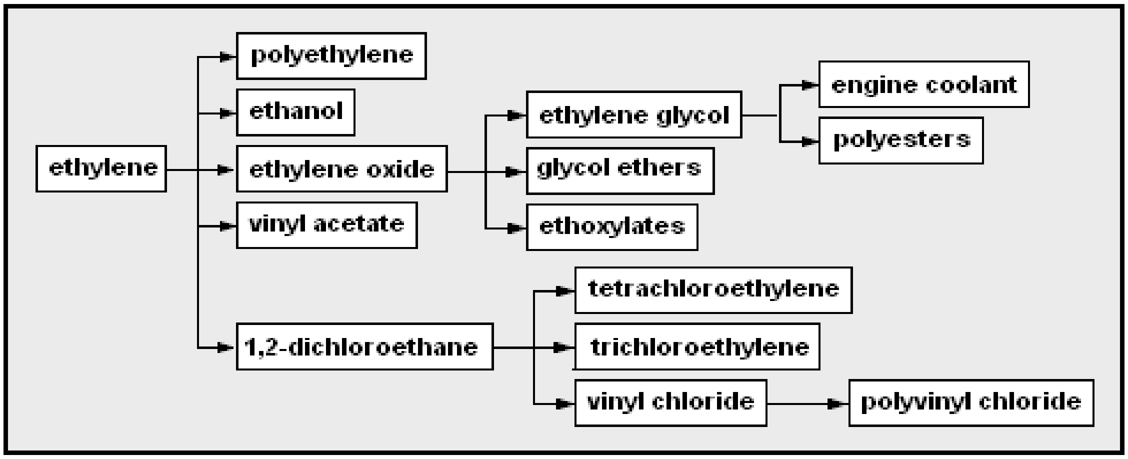
In general, primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered. Natural gas and crude oils are the basic raw materials for the manufacture of petrochemicals.

Secondary raw materials, or intermediates, are obtained from natural gas and crude oils through different processing schemes. The intermediates may be light hydrocarbon compounds such as methane and ethane, or heavier hydrocarbon mixtures such as naphtha or gas oil. Both naphtha and gas oil are crude oil fractions with different boiling ranges.

Coal, oil shale, and tar sand are complex carbonaceous raw materials and possible future energy and chemical sources. However, they must undergo lengthy and extensive processing before they yield fuels and chemicals similar to those produced from crude oils (substitute natural gas (SNG) and synthetic crudes from coal, tar sand and oil shale).

*ethylene:-

- ethylene - the simplest olefin; used as a chemical feedstock and ripening stimulant
- polyethylene - polymerized ethylene; LDPE, HDPE, LLDPE
- ethanol - via ethylene hydration (chemical reaction adding water) of ethylene
- ethylene oxide - via ethylene oxidation
- ethylene glycol - via ethylene oxide hydration
- engine coolant - ethylene glycol, water and inhibitor mixture
- polyesters - any of several polymers with ester linkages in the main chain
- glycol ethers - via glycol condescension
- ethoxylates
- vinyl acetate

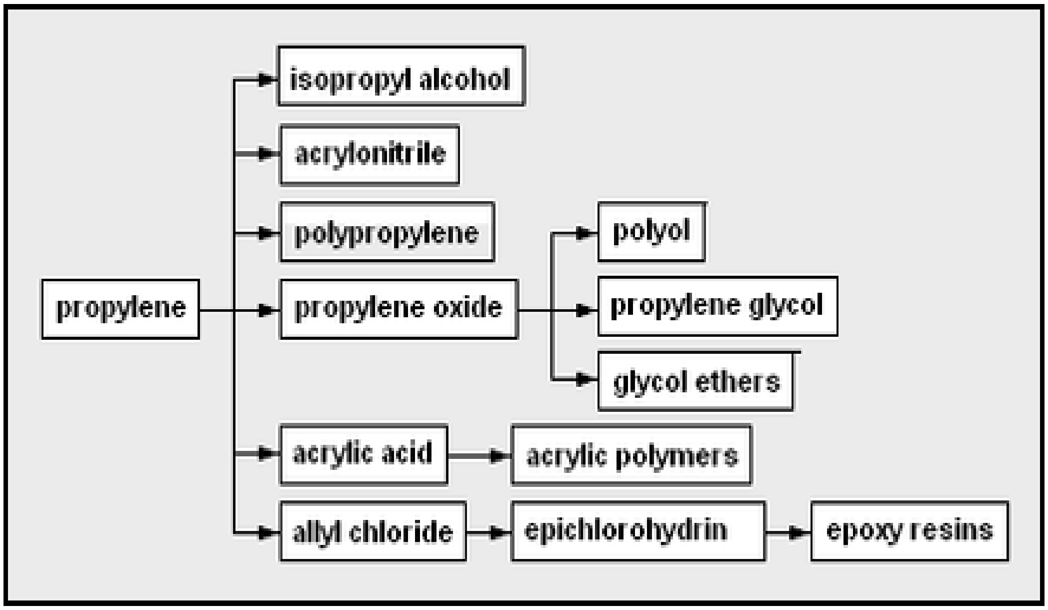


Chemicals produced from ethylene

*propylene:

propylene - used as a monomer and a chemical feedstock

- isopropyl alcohol - 2-propanol; often used as a solvent or rubbing alcohol
- acrylonitrile - useful as a monomer in forming Orlon, ABS
- polypropylene - polymerized propylene
- propylene oxide
    - polyether polyol - used in the production of polyurethanes
    - propylene glycol - used in engine coolant and aircraft deicer fluid
    - glycol ethers - from condensation of glycols
- acrylic acid
    - acrylic polymers
- allyl chloride -
    - epichlorohydrin - chloro-oxirane; used in epoxy resin formation
        - epoxy resins - a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine



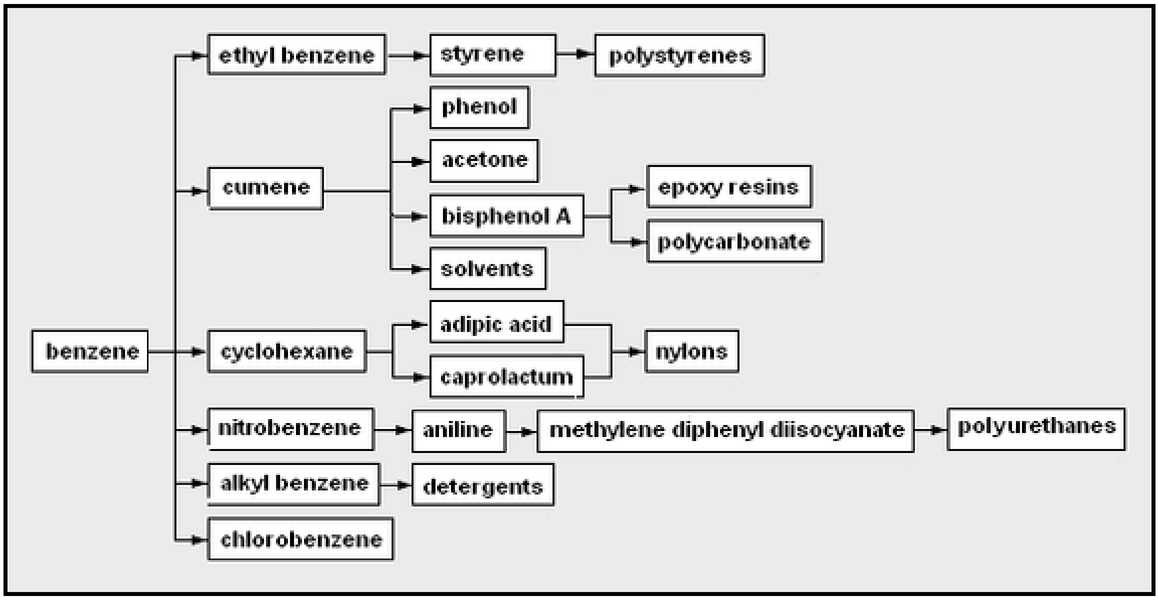
Chemicals produced from propylene

Aromatics (BTX)

*benzene:-

benzene - the simplest aromatic hydrocarbon

- ethylbenzene - made from benzene and ethylene
    - **styrene made by dehydrogenation of ethylbenzene; used as a monomer**
        - polystyrenes - polymers with styrene as a monomer
- cumene - isopropylbenzene; a feedstock in the cumene process
    - phenol - hydroxybenzene; often made by the cumene process
    - acetone - dimethyl ketone; also often made by the cumene process
    - bisphenol A - a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate
        - epoxy resins - a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine
        - polycarbonate - a plastic polymer made from bisphenol A and phosgene (carbonyl dichloride)
    - solvents - liquids used for dissolving materials; examples often made from petrochemicals include ethanol, isopropyl alcohol, acetone, benzene, toluene, xylenes
    - cyclohexane - a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent
        - adipic acid - a 6-carbon dicarboxylic acid, which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon.
            - nylons - types of polyamides, some are alternating copolymers formed from copolymerizing dicarboxylic acid or derivatives with diamines
        - caprolactam - a 6-carbon cyclic amide
            - nylons - types of polyamides, some are from polymerizing caprolactam
    - nitrobenzene - can be made by single nitration of benzene
        - aniline - aminobenzene
            - methylene diphenyl diisocyanate (MDI) - used as a co-monomer with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas
    - alkylbenzene - a general type of aromatic hydrocarbon, which can be used as a presursor for a sulfonate surfactant (detergent)
        - detergents - often include surfactants types such as alkylbenzenesulfonates and nonylphenol ethoxylates
    - chlorobenzene

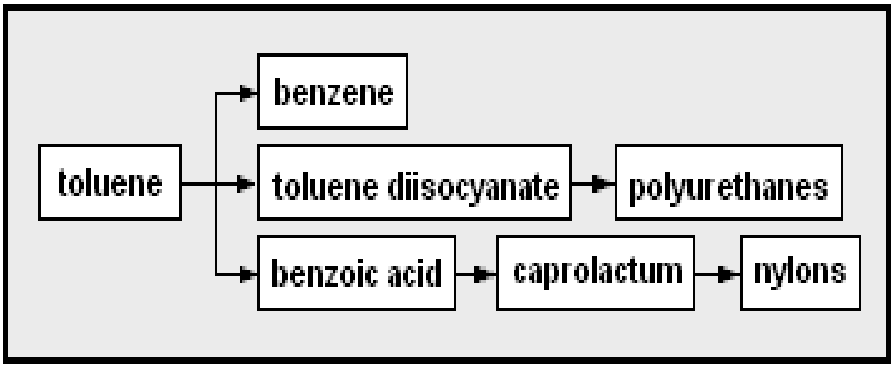


Chemicals produced from benzene

* Toluene

toluene - methylbenzene; can be a solvent or precursor for other chemicals

- benzene
- toluene diisocyanate (TDI) - used as co-monomers with polyether polyols to form polyurethanes or with di- or polyamines to form polyureas polyurethanes
- benzoic acid - carboxybenzene
    - caprolactam
        - nylon

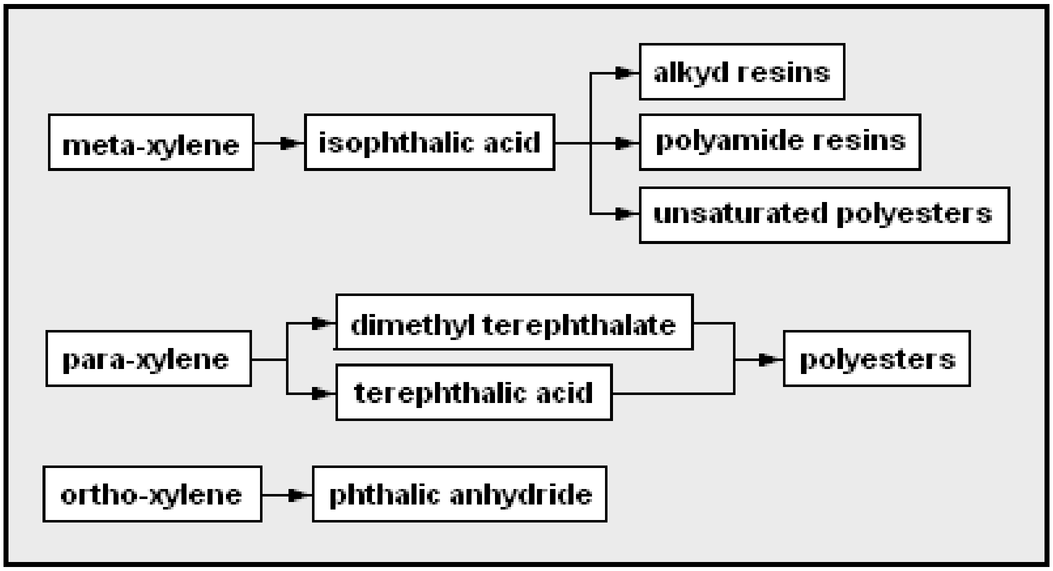


Chemicals produced from toluene

*xylenes:-

mixed xylenes - any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals

- *ortho*-xylene - both methyl groups can be oxidized to form (*ortho*-)phthalic acid
  - phthalic anhydride
- *para*-xylene - both methyl groups can be oxidized to form terephthalic acid
  - dimethyl terephthalate - can be copolymerized to form certain polyesters
    - polyesters - although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.
  - purified terephthalic acid - often copolymerized to form polyethylene terephthalate
    - polyesters
- *meta*-xylene
  - isophthalic acid
    - alkyd resins
    - Polyamide Resins
    - Unsaturated Polyesters



Chemicals produced from xylenes

CHAPTER ONE

Primary Raw Materials for Petrochemicals

INTRODUCTION

In general, primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered. Natural gas and crude oils are the basic raw materials for the manufacture of petrochemicals. The first part of this chapter deals with natural gas. The second part discusses crude oils and their properties.

Secondary raw materials, or intermediates, are obtained from natural gas and crude oils through different processing schemes. The intermediates may be light hydrocarbon compounds such as methane and ethane, or heavier hydrocarbon mixtures such as naphtha or gas oil. Both naphtha and gas oil are crude oil fractions with different boiling ranges. The properties of these intermediates are discussed in Chapter 2.

Coal, oil shale, and tar sand are complex carbonaceous raw materials and possible future energy and chemical sources. However, they must undergo lengthy and extensive processing before they yield fuels and chemicals similar to those produced from crude oils (substitute natural gas (SNG) and synthetic crudes from coal, tar sand and oil shale). These materials are discussed briefly at the end of this chapter.

NATURAL GAS
(Non-associated and Associated Natural Gases)

Natural gas is a naturally occurring mixture of light hydrocarbons accompanied by some non-hydrocarbon compounds. Non-associated natural gas is found in reservoirs containing no oil (dry wells). Associated gas, on the other hand, is present in contact with and/or dissolved in crude oil and is coproduced with it. The principal component of most

Table 1-1
Composition of non-associated and associated natural gases[1]

	Non-associated gas		Associated gas	
Component	Salt Lake US	Kliffside US	Abqaiq Saudi Arabia	North Sea UK
Methane	95.0	65.8	62.2	85.9
Ethane	0.8	3.8	15.1	8.1
Propane	0.2	1.7	6.6	2.7
Butanes	—	0.8	2.4	0.9
Pentane and Heavier	—	0.5	1.1	0.3
Hydrogen sulfide	—	—	2.8	—
Carbon dioxide	3.6	—	9.2	1.6
Nitrogen	0.4	25.6	—	0.5
Helium	—	1.8	—	—

natural gases is methane. Higher molecular weight paraffinic hydrocarbons (C_2-C_7) are usually present in smaller amounts with the natural gas mixture, and their ratios vary considerably from one gas field to another. Non-associated gas normally contains a higher methane ratio than associated gas, while the latter contains a higher ratio of heavier hydrocarbons. Table 1-1 shows the analyses of some selected non-associated and associated gases.[1] In our discussion, both non-associated and associated gases will be referred to as natural gas. However, important differences will be noted.

The non-hydrocarbon constituents in natural gas vary appreciably from one gas field to another. Some of these compounds are weak acids, such as hydrogen sulfide and carbon dioxide. Others are inert, such as nitrogen, helium and argon. Some natural gas reservoirs contain enough helium for commercial production.

Higher molecular weight hydrocarbons present in natural gases are important fuels as well as chemical feedstocks and are normally recovered as natural gas liquids. For example, ethane may be separated for use as a feedstock for steam cracking for the production of ethylene. Propane and butane are recovered from natural gas and sold as liquefied petroleum gas (LPG). Before natural gas is used it must be processed or treated to remove the impurities and to recover the heavier hydrocarbons (heavier than methane). The 1998 U.S. gas consumption was approximately 22.5 trillion ft^3.

NATURAL GAS TREATMENT PROCESSES

Raw natural gases contain variable amounts of carbon dioxide, hydrogen sulfide, and water vapor. The presence of hydrogen sulfide in natural gas for domestic consumption cannot be tolerated because it is poisonous. It also corrodes metallic equipment. Carbon dioxide is undesirable, because it reduces the heating value of the gas and solidifies under the high pressure and low temperatures used for transporting natural gas. For obtaining a sweet, dry natural gas, acid gases must be removed and water vapor reduced. In addition, natural gas with appreciable amounts of heavy hydrocarbons should be treated for their recovery as natural gas liquids.

Acid Gas Treatment

Acid gases can be reduced or removed by one or more of the following methods:

1. Physical absorption using a selective absorption solvent.
2. Physical adsorption using a solid adsorbent.
3. Chemical absorption where a solvent (a chemical) capable of reacting reversibly with the acid gases is used.

Physical Absorption

Important processes commercially used are the Selexol, the Sulfinol, and the Rectisol processes. In these processes, no chemical reaction occurs between the acid gas and the solvent. The solvent, or absorbent, is a liquid that selectively absorbs the acid gases and leaves out the hydrocarbons. In the Selexol process for example, the solvent is dimethyl ether of polyethylene glycol. Raw natural gas passes countercurrently to the descending solvent. When the solvent becomes saturated with the acid gases, the pressure is reduced, and hydrogen sulfide and carbon dioxide are desorbed. The solvent is then recycled to the absorption tower. Figure 1-1 shows the Selexol process.[2]

Physical Adsorption

In these processes, a solid with a high surface area is used. Molecular sieves (zeolites) are widely used and are capable of adsorbing large amounts of gases. In practice, more than one adsorption bed is used for continuous operation. One bed is in use while the other is being regenerated.

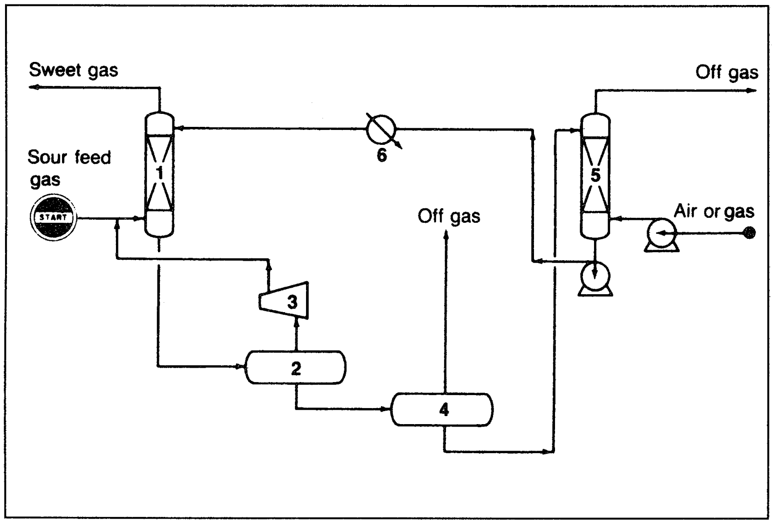


Figure 1-1. The Selexol process for acid gas removal:[2] (1) absorber, (2) flash drum, (3) compressor, (4) low-pressure drum, (5) stripper, (6) cooler.

Regeneration is accomplished by passing hot dry fuel gas through the bed. Molecular sieves are competitive only when the quantities of hydrogen sulfide and carbon disulfide are low.

Molecular sieves are also capable of adsorbing water in addition to the acid gases.

Chemical Absorption (Chemisorption)

These processes are characterized by a high capability of absorbing large amounts of acid gases. They use a solution of a relatively weak base, such as monoethanolamine. The acid gas forms a weak bond with the base which can be regenerated easily. Mono- and diethanolamines are frequently used for this purpose. The amine concentration normally ranges between 15 and 30%. Natural gas is passed through the amine solution where sulfides, carbonates, and bicarbonates are formed.

Diethanolamine is a favored absorbent due to its lower corrosion rate, smaller amine loss potential, fewer utility requirements, and minimal reclaiming needs.[3] Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS), while the mono- reacts irreversibly with 95% of the COS and forms a degradation product that must be disposed of.

Diglycolamine (DGA), is another amine solvent used in the Econamine process (Fig 1-2).[4] Absorption of acid gases occurs in an absorber containing an aqueous solution of DGA, and the heated rich

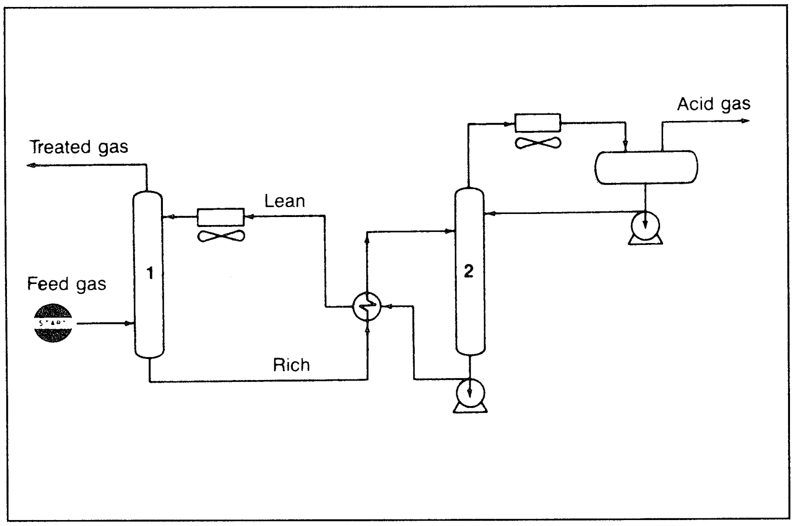


Figure 1-2. The Econamine process:[4] (1) absorption tower, (2) regeneration tower.

solution (saturated with acid gases) is pumped to the regenerator. Diglycolamine solutions are characterized by low freezing points, which make them suitable for use in cold climates.

Strong basic solutions are effective solvents for acid gases. However, these solutions are not normally used for treating large volumes of natural gas because the acid gases form stable salts, which are not easily regenerated. For example, carbon dioxide and hydrogen sulfide react with aqueous sodium hydroxide to yield sodium carbonate and sodium sulfide, respectively.

$$CO_2 + 2NaOH_{(aq)} \rightarrow Na_2CO_3 + H_2O$$

$$H_2S + 2\,NaOH_{(aq)} \rightarrow Na_2S + 2\,H_2O$$

However, a strong caustic solution is used to remove mercaptans from gas and liquid streams. In the Merox Process, for example, a caustic solvent containing a catalyst such as cobalt, which is capable of converting mercaptans (RSH) to caustic insoluble disulfides (RSSR), is used for streams rich in mercaptans after removal of H_2S. Air is used to oxidize the mercaptans to disulfides. The caustic solution is then recycled for regeneration. The Merox process (Fig. 1-3) is mainly used for treatment of refinery gas streams.[5]

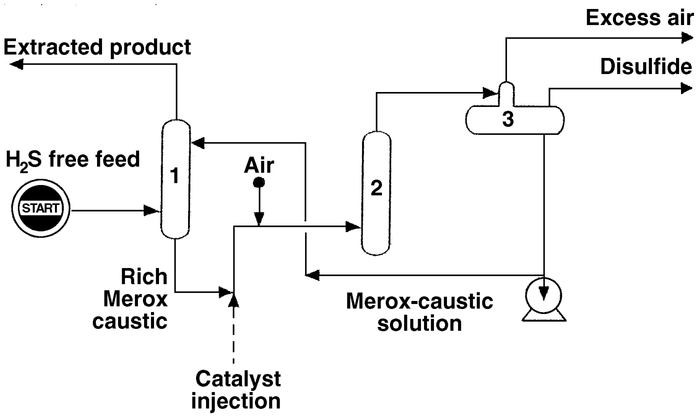


Figure 1-3. The Merox process:[5] (1) extractor, (2) oxidation reactor.

Water Removal

Moisture must be removed from natural gas to reduce corrosion problems and to prevent hydrate formation. Hydrates are solid white compounds formed from a physical-chemical reaction between hydrocarbons and water under the high pressures and low temperatures used to transport natural gas via pipeline. Hydrates reduce pipeline efficiency.

To prevent hydrate formation, natural gas may be treated with glycols, which dissolve water efficiently. Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) are typical solvents for water removal. Triethylene glycol is preferable in vapor phase processes because of its low vapor pressure, which results in less glycol loss. The TEG absorber normally contains 6 to 12 bubble-cap trays to accomplish the water absorption. However, more contact stages may be required to reach dew points below –40°F. Calculations to determine the number of trays or feet of packing, the required glycol concentration, or the glycol circulation rate require vapor-liquid equilibrium data. Predicting the interaction between TEG and water vapor in natural gas over a broad range allows the designs for ultra-low dew point applications to be made.[6]

A computer program was developed by Grandhidsan et al., to estimate the number of trays and the circulation rate of lean TEG needed to dry natual gas. It was found that more accurate predictions of the rate could be achieved using this program than using hand calculation.[7]

Figure 1-4 shows the Dehydrate process where EG, DEG, or TEG could be used as an absorbent.[8] One alternative to using bubble-cap trays

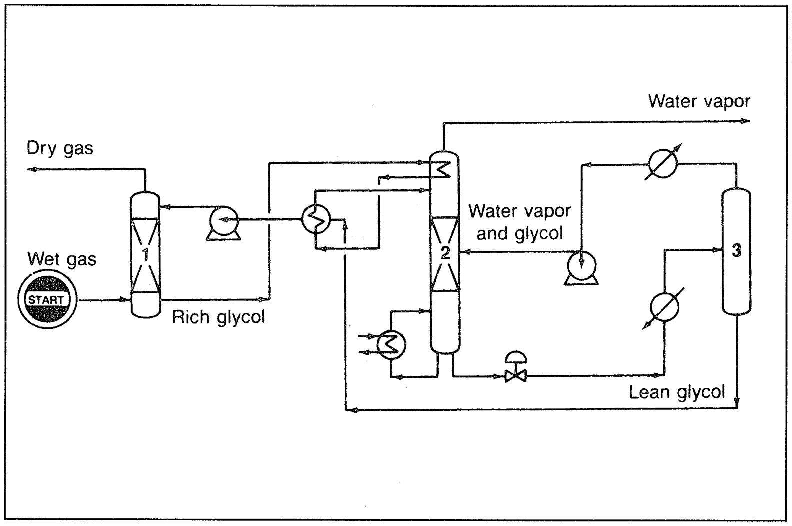


Figure 1-4. Flow diagram of the Dehydrate process[8]: (1) absorption column, (2) glycol sill, (3) vacuum drum.

is structural packing, which improves control of mass transfer. Flow passages direct the gas and liquid flows countercurrent to each other. The use of structural packing in TEG operations has been reviewed by Kean et al.[9]

Another way to dehydrate natural gas is by injecting methanol into gas lines to lower the hydrate-formation temperature below ambient.[10] Water can also be reduced or removed from natural gas by using solid adsorbents such as molecular sieves or silica gel.

Condensable Hydrocarbon Recovery

Hydrocarbons heavier than methane that are present in natural gases are valuable raw materials and important fuels. They can be recovered by lean oil extraction. The first step in this scheme is to cool the treated gas by exchange with liquid propane. The cooled gas is then washed with a cold hydrocarbon liquid, which dissolves most of the condensable hydrocarbons. The uncondensed gas is dry natural gas and is composed mainly of methane with small amounts of ethane and heavier hydrocarbons. The condensed hydrocarbons or natural gas liquids (NGL) are stripped from the rich solvent, which is recycled. Table 1-2 compares the analysis of natural gas before and after treatment.[11] Dry natural gas may then be used either as a fuel or as a chemical feedstock.

Another way to recover NGL is through cryogenic cooling to very low temperatures (–150 to –180°F), which are achieved primarily through

Table 1-2
Typical analysis of natural gas before and after treatment[11]

Component mole %	Feed	Pipeline gas
N_2	0.45	0.62
CO_2	27.85	3.50
H_2S	0.0013	—
C_1	70.35	94.85
C_2	0.83	0.99
C_3	0.22	0.003
C_4	0. 13	0.004
C_5	0.06	0.004
C_{6+}	0.11	0.014

adiabatic expansion of the inlet gas. The inlet gas is first treated to remove water and acid gases, then cooled via heat exchange and refrigeration. Further cooling of the gas is accomplished through turbo expanders, and the gas is sent to a demethanizer to separate methane from NGL. Improved NGL recovery could be achieved through better control strategies and use of on-line gas chromatographic analysis.[12]

NATURAL GAS LIQUIDS (NGL)

Natural gas liquids (condensable hydrocarbons) are those hydrocarbons heavier than methane that are recovered from natural gas. The amount of NGL depends mainly on the percentage of the heavier hydrocarbons present in the gas and on the efficiency of the process used to recover them. (A high percentage is normally expected from associated gas.)

Natural gas liquids are normally fractionated to separate them into three streams:

1. An ethane-rich stream, which is used for producing ethylene.
2. Liquefied petroleum gas (LPG), which is a propane-butane mixture. It is mainly used as a fuel or a chemical feedstock. Liquefied petroleum gas is evolving into an important feedstock for olefin production. It has been predicted that the world (LPG) market for chemicals will grow from 23.1 million tons consumed in 1988 to 36.0 million tons by the year 2000.[13]
3. Natural gasoline (NG) is mainly constituted of $C5^+$ hydrocarbons and is added to gasoline to raise its vapor pressure. Natural gasoline is usually sold according to its vapor pressure.

Natural gas liquids may contain significant amounts of cyclohexane, a precursor for nylon 6 (Chapter 10). Recovery of cyclohexane from NGL by conventional distillation is difficult and not economical because heptane isomers are also present which boil at temperatures nearly identical to that of cyclohexane. An extractive distillation process has been recently developed by Phillips Petroleum Co. to separate cyclohexane.[14]

Liquefied Natural Gas (LNG)

After the recovery of natural gas liquids, sweet dry natural gas may be liquefied for transportation through cryogenic tankers. Further treatment may be required to reduce the water vapor below 10 ppm and carbon dioxide and hydrogen sulfide to less than 100 and 50 ppm, respectively.

Two methods are generally used to liquefy natural gas: the expander cycle and mechanical refrigeration. In the expander cycle, part of the gas is expanded from a high transmission pressure to a lower pressure. This lowers the temperature of the gas. Through heat exchange, the cold gas cools the incoming gas, which in a similar way cools more incoming gas until the liquefaction temperature of methane is reached. Figure 1-5 is a flow diagram for the expander cycle for liquefying natural gas.[15]

In mechanical refrigeration, a multicomponent refrigerant consisting of nitrogen, methane, ethane, and propane is used through a cascade cycle. When these liquids evaporate, the heat required is obtained from

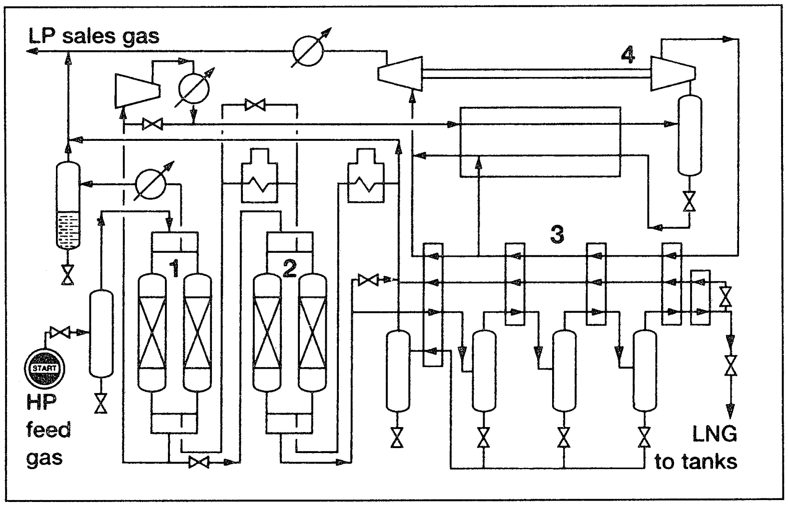


Figure 1-5. Flow diagram of the expander cycle for liquefying natural gas:[15] (1) pretreatment (mol.sieve), (2) heat exchanger, (3) turboexpander.

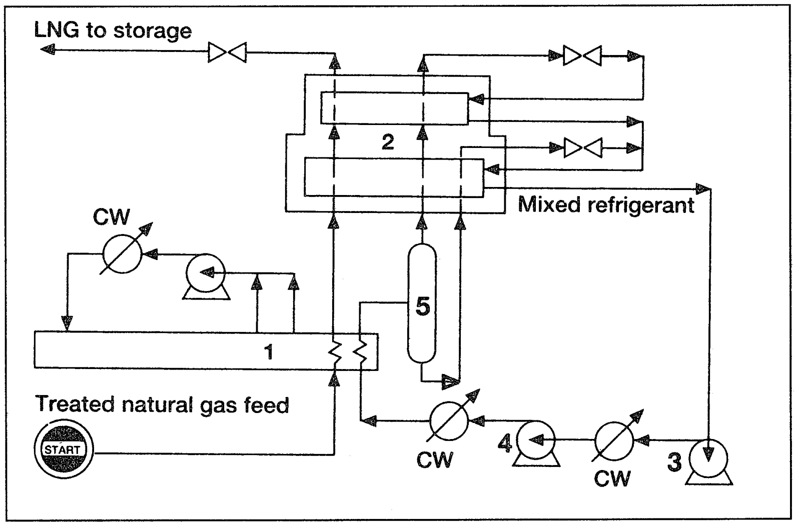


Figure 1-6. The MCR process for liquefying natural gas:[15] (1) coolers, (2) heat exchangers, (3,4) two stage compressors, (5) liquid-vapor phase separator.

natural gas, which loses energy/temperature till it is liquefied. The refrigerant gases are recompressed and recycled. Figure 1-6 shows the MCR natural gas liquefaction process.[15] Table 1-3 lists important properties of a representative liquefied natural gas mixture.

PROPERTIES OF NATURAL GAS

Treated natural gas consists mainly of methane; the properties of both gases (natural gas and methane) are nearly similar. However, natural gas is not pure methane, and its properties are modified by the presence of impurities, such as N_2 and CO_2 and small amounts of unrecovered heavier hydrocarbons.

Table 1-3
Important properties of a representative liquefied natural gas mixture

Density, lb/cf	27.00
Boiling point, °C	–158
Calorific value, Btu/lb	21200
Specific volume, cf/lb	0.037
Critical temperature, °C*	–82.3
Critical pressure, psi*	–673

* Critical temperature and pressure for pure liquid methane.

An important property of natural gas is its heating value. Relatively high amounts of nitrogen and/or carbon dioxide reduce the heating value of the gas. Pure methane has a heating value of 1,009 Btu/ft^3. This value is reduced to approximately 900 Btu/ft3 if the gas contains about 10% N_2 and CO_2. (The heating value of either nitrogen or carbon dioxide is zero.) On the other hand, the heating value of natural gas could exceed methane's due to the presence of higher-molecular weight hydrocarbons, which have higher heating values. For example, ethane's heating value is 1,800 Btu/ft^3, compared to 1,009 Btu/ft^3 for methane. Heating values of hydrocarbons normally present in natural gas are shown in Table 1-4.

Natural gas is usually sold according to its heating values. The heating value of a product gas is a function of the constituents present in the mixture. In the natural gas trade, a heating value of one million Btu is approximately equivalent to 1,000 ft^3 of natural gas.

CRUDE OILS

Crude oil (petroleum) is a naturally occurring brown to black flammable liquid. Crude oils are principally found in oil reservoirs associated with sedimentary rocks beneath the earth's surface. Although exactly how crude oils originated is not established, it is generally agreed that crude oils derived from marine animal and plant debris subjected to high temperatures and pressures. It is also suspected that the transformation may have been catalyzed by rock constituents. Regardless of their origins,

Table 1-4
Heating values of methane and heavier hydrocarbons present in natural gas

Hydrocarbon	Formula	Heating value Btu/ft^3
Methane	CH_4	1,009
Ethane	C_2H_6	1,800
Propane	C_3H_8	2,300
Isobutane	C_4H_{10}	3,253
n-Butane	C_4H_{10}	3,262
Isopentane	C_5H_{12}	4,000
n-Pentane	C_5H_{12}	4,010
n-Hexane	C_6H_{14}	4,750
n-Heptane	C_7H_{16}	5,502

all crude oils are mainly constituted of hydrocarbons mixed with variable amounts of sulfur, nitrogen, and oxygen compounds.

Metals in the forms of inorganic salts or organometallic compounds are present in the crude mixture in trace amounts. The ratio of the different constituents in crude oils, however, vary appreciably from one reservoir to another.

Normally, crude oils are not used directly as fuels or as feedstocks for the production of chemicals. This is due to the complex nature of the crude oil mixture and the presence of some impurities that are corrosive or poisonous to processing catalysts.

Crude oils are refined to separate the mixture into simpler fractions that can be used as fuels, lubricants, or as intermediate feedstock to the petrochemical industries. A general knowledge of this composite mixture is essential for establishing a processing strategy.

COMPOSITION OF CRUDE OILS

The crude oil mixture is composed of the following groups:

1. Hydrocarbon compounds (compounds made of carbon and hydrogen).
2. Non-hydrocarbon compounds.
3. Organometallic compounds and inorganic salts (metallic compounds).

Hydrocarbon Compounds

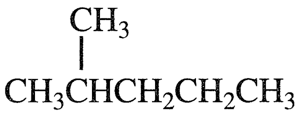
The principal constituents of most crude oils are hydrocarbon compounds. All hydrocarbon classes are present in the crude mixture, except alkenes and alkynes. This may indicate that crude oils originated under a reducing atmosphere. The following is a brief description of the different hydrocarbon classes found in all crude oils.

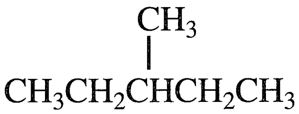
Alkanes (Paraffins)

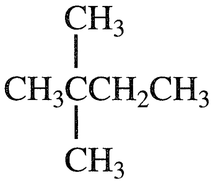
Alkanes are saturated hydrocarbons having the general formula C_nH_{2n+2}. The simplest alkane, methane (CH_4), is the principal constituent of natural gas. Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oils in a dissolved state.

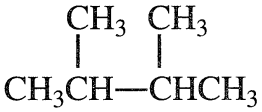
Normal alkanes (n-alkanes, n-paraffins) are straight-chain hydrocarbons having no branches. Branched alkanes are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain. A branched alkane with the same number of carbons and hydrogens as an n-alkane is called an isomer. For example, butane (C_4H_{10}) has two isomers, n-butane and 2-methyl propane (isobutane). As the molecular weight of the hydrocarbon increases, the number of isomers also increases. Pentane (C_5C_{12}) has three isomers; hexane (C_6H_{14}) has five. The following shows the isomers of hexane:

$CH_3(CH_2)_4CH_3$
n-Hexane


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$
2-Methylpentane
(Isohexane)


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$
3-Methylpentane

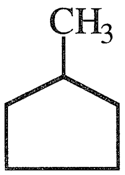

$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_3$
2,2-Dimethylbutane

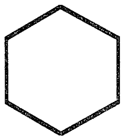

$CH_3\overset{CH_3}{\overset{|}{C}}H{-}\overset{CH_3}{\overset{|}{C}}HCH_3$
2,3-Dimethylbutane

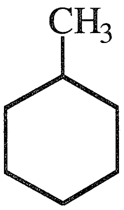
An isoparaffin is an isomer having a methyl group branching from carbon number 2 of the main chain. Crude oils contain many short, medium, and long-chain normal and branched paraffins. A naphtha fraction (obtained as a light liquid stream from crude fractionation) with a narrow boiling range may contain a limited but still large number of isomers.

Cycloparaffins (Naphthenes)

Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds. They are normally present in the light and the heavy naphtha fractions. Cyclohexanes, substituted cyclopentanes, and substituted cyclohexanes are important precursors for aromatic hydrocarbons.


Methylcyclopentane


Cyclohexane


Methylcyclohexane

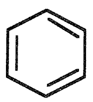
The examples shown here are for three naphthenes of special importance. If a naphtha fraction contains these compounds, the first two can be converted to benzene, and the last compound can dehydrogenate to toluene during processing. Dimethylcyclohexanes are also important precursors for xylenes (see "Xylenes" later in this section).

Heavier petroleum fractions such as kerosine and gas oil may contain two or more cyclohexane rings fused through two vicinal carbons.

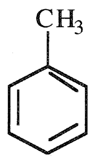
Aromatic Compounds

Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions. The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils. Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components. Separating BTX aromatics from crude oil distillates is not feasible because they are present in low concentrations. Enriching a naphtha fraction with these aromatics is possible through a catalytic reforming process. Chapter 3 discusses catalytic reforming.

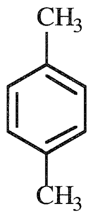
Binuclear aromatic hydrocarbons are found in heavier fractions than naphtha. Trinuclear and polynuclear aromatic hydrocarbons, in combination with heterocyclic compounds, are major constituents of heavy crudes and crude residues. Asphaltenes are a complex mixture of aromatic and heterocyclic compounds. The nature and structure of some of these compounds have been investigated.[16] The following are representative examples of some aromatic compounds found in crude oils:



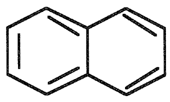
Benzene



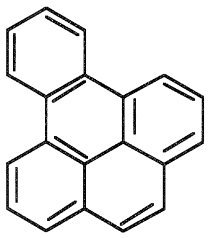
Toluene



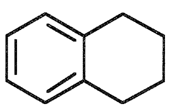
p-Xylene



Naphthalene



1,2-Benzopyrene



Tetralin

Only a few aromatic-cycloparaffin compounds have been isolated and identified. Tetralin is an example of this class.

Non-hydrocarbon Compounds

Various types of non-hydrocarbon compounds occur in crude oils and refinery streams. The most important are the organic sulfur, nitrogen, and oxygen compounds. Traces of metallic compounds are also found in all crudes. The presence of these impurities is harmful and may cause problems to certain catalytic processes. Fuels having high sulfur and nitrogen levels cause pollution problems in addition to the corrosive nature of their oxidization products.

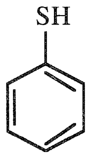
Sulfur Compounds

Sulfur in crude oils is mainly present in the form of organosulfur compounds. Hydrogen sulfide is the only important inorganic sulfur compound found in crude oil. Its presence, however, is harmful because of its corrosive nature. Organosulfur compounds may generally be classified as acidic and non-acidic. Acidic sulfur compounds are the thiols (mercaptans). Thiophene, sulfides, and disulfides are examples of non-acidic sulfur compounds found in crude fractions. Extensive research has been carried out to identify some sulfur compounds in a narrow light petroleum fraction.[17] Examples of some sulfur compounds from the two types are:

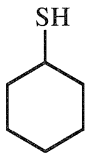
Acidic Sulfur Compounds

CH_3SH

Methyl mercaptan



Phenyl mercaptan



Cyclohexylthiol

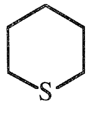
Non-acidic Sulfur Compounds

CH_3SCH_3

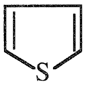
Dimethyl sulfide

$CH_3S\text{-}SCH_3$

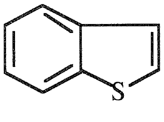
Dimethyldisulfide



Thiocyclohexane



Thiophene



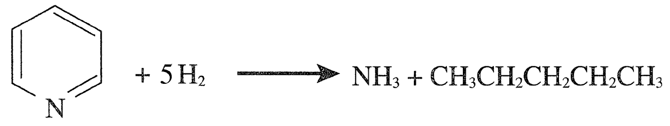
Benzothiophene

Sour crudes contain a high percentage of hydrogen sulfide. Because many organic sulfur compounds are not thermally stable, hydrogen sulfide is often produced during crude processing. High-sulfur crudes are less desirable because treating the different refinery streams for acidic hydrogen sulfide increases production costs.

Most sulfur compounds can be removed from petroleum streams through hydrotreatment processes, where hydrogen sulfide is produced and the corresponding hydrocarbon released. Hydrogen sulfide is then absorbed in a suitable absorbent and recovered as sulfur (Chapter 4).

Nitrogen Compounds

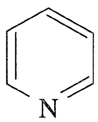
Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin. The nitrogen content in most crudes is very low and does not exceed 0.1 wt%. In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt %.[18] Nitrogen compounds are more thermally stable than sulfur compounds and accordingly are concentrated in heavier petroleum fractions and residues. Light petroleum streams may contain trace amounts of nitrogen compounds, which should be removed because they poison many processing catalysts. During hydrotreatment of petroleum fractions, nitrogen compounds are hydrodenitrogenated to ammonia and the corresponding hydrocarbon. For example, pyridine is denitrogenated to ammonia and pentane:



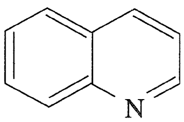
Nitrogen compounds in crudes may generally be classified into basic and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure. Both pyridine and pyrrole are stable compounds due to their aromatic nature.

The following are examples of organic nitrogen compounds.

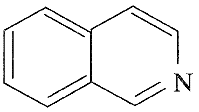
Basic Nitrogen Compounds



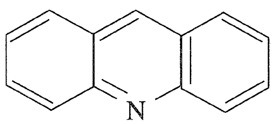
Pyridine



Quinoline

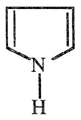


Isoquinoline

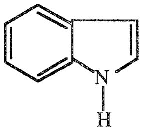


Acridine

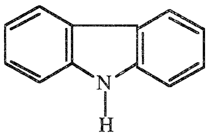
Non-Basic Nitrogen Compounds



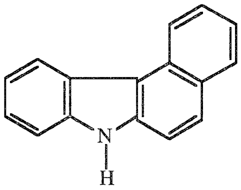
Pyrrole



Indole

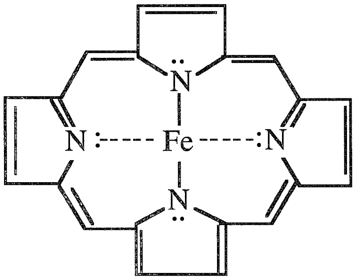


Carbazole



Benzocarbazole

Porphyrins are non-basic nitrogen compounds. The porphyrin ring system is composed of four pyrrole rings joined by =CH-groups. The entire ring system is aromatic. Many metal ions can replace the pyrrole hydrogens and form chelates. The chelate is planar around the metal ion and resonance results in four equivalent bonds from the nitrogen atoms to the metal.[19] Almost all crude oils and bitumens contain detectable amounts of vanadyl and nickel porphyrins. The following shows a porphyrin structure:



Separation of nitrogen compounds is difficult, and the compounds are susceptible to alteration and loss during handling. However, the basic low-molecular weight compounds may be extracted with dilute mineral acids.

Oxygen Compounds

Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts. Many of the oxygen compounds found in crude oils are weakly acidic. They are carboxylic acids, cresylic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain.

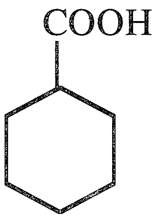
Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crudes is generally low, but may reach as much as 3%, as in some California crudes.

Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds. They are of no commercial value. The following shows some of the oxygen compounds commonly found in crude oils:

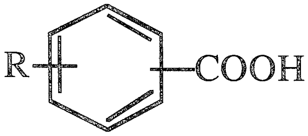
Acidic Oxygen Compounds

$CH_3(CH_2)_nCOOH$

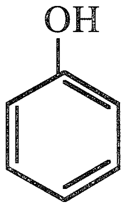
An aliphatic carboxylic acid



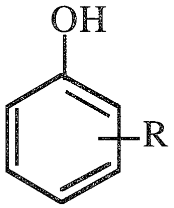
Cyclohexane carboxylic acid



Aromatic acids



Phenol



Cresylic acid

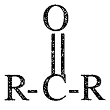
Non-Acidic Oxygen Compounds

R-COOR'

Esters

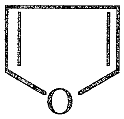
R-CONHR'

Amides

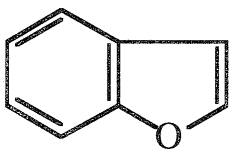


$R-\overset{\displaystyle O}{\overset{\|}{C}}-R$

Ketone



Furan



Benzofuran

Metallic Compounds

Many metals occur in crude oils. Some of the more abundant are sodium, calcium, magnesium, aluminium, iron, vanadium, and nickel. They are present either as inorganic salts, such as sodium and magnesium chlorides, or in the form of organometallic compounds, such as those of nickel and vanadium (as in porphyrins). Calcium and magnesium can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable.

Although metals in crudes are found in trace amounts, their presence is harmful and should be removed. When crude oil is processed, sodium and magnesium chlorides produce hydrochloric acid, which is very corrosive. Desalting crude oils is a necessary step to reduce these salts.

Vanadium and nickel are poisons to many catalysts and should be reduced to very low levels. Most of the vanadium and nickel compounds are concentrated in the heavy residues. Solvent extraction processes are used to reduce the concentration of heavy metals in petroleum residues.

PROPERTIES OF CRUDE OILS

Crude oils differ appreciably in their properties according to origin and the ratio of the different components in the mixture. Lighter crudes generally yield more valuable light and middle distillates and are sold at higher prices. Crudes containing a high percent of impurities, such as sulfur compounds, are less desirable than low-sulfur crudes because of their corrosivity and the extra treating cost. Corrosivity of crude oils is a function of many parameters among which are the type of sulfur compounds and their decomposition temperatures, the total acid number, the type of carboxylic and naphthenic acids in the crude and their decomposition temperatures. It was found that naphthenic acids begin to decompose at 600°F. Refinery experience has shown that above 750°F there is no naphthenic acid corrosion. The subject has been reviewed by Kane and Cayard.[20] For a refiner, it is necessary to establish certain criteria to relate one crude to another to be able to assess crude quality and choose the best processing scheme. The following are some of the important tests used to determine the properties of crude oils.

Density, Specific Gravity and API Gravity

Density is defined as the mass of unit volume of a material at a specific temperature. A more useful unit used by the petroleum industry is specific gravity, which is the ratio of the weight of a given volume of a material to the weight of the same volume of water measured at the same temperature.

Specific gravity is used to calculate the mass of crude oils and its products. Usually, crude oils and their liquid products are first measured on a volume basis, then changed to the corresponding masses using the specific gravity.

The API (American Petroleum Institute) gravity is another way to express the relative masses of crude oils. The API gravity could be calculated mathematically using the following equation:

$$^\circ\mathrm{API} = \frac{141.5}{\mathrm{Sp.gr.}\ 60/60^\circ} - 131.5$$

A low API gravity indicates a heavier crude oil or a petroleum product, while a higher API gravity means a lighter crude or product. Specific gravities of crude oils roughly range from 0.82 for lighter crudes to over 1.0 for heavier crudes (41 - 10 °API scale).

Salt Content

The salt content expressed in milligrams of sodium chloride per liter oil (or in pounds/barrel) indicates the amount of salt dissolved in water. Water in crudes is mainly present in an emulsified form. A high salt content in a crude oil presents serious corrosion problems during the refining process. In addition, high salt content is a major cause of plugging heat exchangers and heater pipes. A salt content higher than 10 lb/1,000 barrels (expressed as NaCl) requires desalting.

Sulfur Content

Determining the sulfur content in crudes is important because the amount of sulfur indicates the type of treatment required for the distillates. To determine sulfur content, a weighed crude sample (or fraction) is burned in an air stream. All sulfur compounds are oxidized to sulfur dioxide, which is further oxidized to sulfur trioxide and finally titrated with a standard alkali.

Identifying sulfur compounds in crude oils and their products is of little use to a refiner because all sulfur compounds can easily be hydrodesulfurized to hydrogen sulfide and the corresponding hydrocarbon.

The sulfur content of crudes, however, is important and is usually considered when determining commercial values.

Pour Point

The pour point of a crude oil or product is the lowest temperature at which an oil is observed to flow under the conditions of the test. Pour point data indicates the amount of long-chain paraffins (petroleum wax) found in a crude oil. Paraffinic crudes usually have higher wax content than other crude types. Handling and transporting crude oils and heavy fuels is difficult at temperatures below their pour points Often, chemical additives known as pour point depressants are used to improve the flow properties of the fuel. Long-chain n-paraffins ranging from 16–60 carbon atoms in particular, are responsible for near-ambient temperature precipitation. In middle distillates, less than 1% wax can be sufficient to cause solidification of the fuel.[21]

Ash Content

This test indicates the amount of metallic constituents in a crude oil. The ash left after completely burning an oil sample usually consists of stable metallic salts, metal oxides, and silicon oxide. The ash could be further analyzed for individual elements using spectroscopic techniques.

CRUDE OIL CLASSIFICATION

Appreciable property differences appear between crude oils as a result of the variable ratios of the crude oil components. For a refiner dealing with crudes of different origins, a simple criterion may be established to group crudes with similar characteristics. Crude oils can be arbitrarily classified into three or four groups depending on the relative ratio of the hydrocarbon classes that predominates in the mixture. The following describes three types of crudes:

1. Paraffinic—the ratio of paraffinic hydrocarbons is high compared to aromatics and naphthenes.
2. Naphthenic—the ratios of naphthenic and aromatic hydrocarbons are relatively higher than in paraffinic crudes.
3. Asphaltic—contain relatively a large amount of polynuclear aromatics, a high asphaltene content, and relatively less paraffins than paraffinic crudes.

A correlation index is a useful criterion for indicating the crude class or type. The following relationship between the mid-boiling point in Kelvin degrees (°K) and the specific gravity of a crude oil or a fraction yields the correlation index (Bureau of Mines Correlation index).[22]

$$\text{BMCI} = 48{,}640 / K + (473.6d - 456.8)$$

K = mid-boiling point in Kelvin degrees (Mid-boiling point is the temperature at which 50 vol % of the crude is distilled.)
d = specific gravity at 60/60°F

A zero value has been assumed for n-paraffins, 100 for aromatics. A low BMCI value indicates a higher paraffin concentration in a petroleum fraction.

Another relationship used to indicate the crude type is the Watson characterization factor. The factor also relates the mid-boiling point of the crude or a fraction to the specific gravity.

$$\text{Watson characterization factor} = \frac{T^{1/3}}{d}$$

where T = mid-boiling point in °R (°R is the absolute °F, and equals °F + 460)

A value higher than 10 indicates a predominance of paraffins while a value around 10 means a predominance of aromatics.

Table 1-5
Typical analysis of some crude oils

	Arab Extra Light*	Alameen Egypt	Arab Heavy	Bakr-9 Egypt
Gravity, °API	38.5	33.4	28.0	20.9
Carbon residue (wt %)	2.0	5.1	6.8	11.7
Sulfur content (wt %)	1.1	0.86	2.8	3.8
Nitrogen content (wt %)	0.04	0.12	0.15	—
Ash content (wt %)	0.002	0.004	0.012	0.04
Iron (ppm)	0.4	0.0	1.0	—
Nickel (ppm)	0.6	0.0	9.0	108
Vanadium (ppm)	2.2	15	40.0	150
Pour point (°F)	≈Zero	35	–11.0	55
Paraffin wax content (wt %)	—	3.3	—	—

* Ali, M. F et al., Hydrocarbon Processing, Vol. 64, No. 2, 1985 p. 83.

Properties of crude oils vary considerably according to their types. Table 1-5 lists the analyses of some crudes from different origins.

COAL, OIL SHALE, TAR SAND, AND GAS HYDRATES

Coal, oil shale, and tar sand are carbonaceous materials that can serve as future energy and chemical sources when oil and gas are consumed. The H/C ratio of these materials is lower than in most crude oils. As solids or semi-solids, they are not easy to handle or to use as fuels, compared to crude oils. In addition, most of these materials have high sulfur and/or nitrogen contents, which require extensive processing. Changing these materials into hydrocarbon liquids or gaseous fuels is possible but expensive. The following briefly discusses these alternative energy and chemical sources.

COAL

Coal is a natural combustible rock composed of an organic heterogeneous substance contaminated with variable amounts of inorganic compounds. Most coal reserves are concentrated in North America, Europe, and China.

Coal is classified into different ranks according to the degree of chemical change that occurred during the decomposition of plant remains in the prehistoric period. In general, coals with a high heating value and a high fixed carbon content are considered to have been subjected to more severe changes than those with lower heating values and fixed carbon contents. For example, peat, which is considered a young coal, has a low fixed carbon content and a low heating value. Important coal ranks are anthracite (which has been subjected to the most chemical change and is mostly carbon), bituminous coal, sub-bituminous coal, and lignite. Table 1-6 compares the analysis of some coals with crude oil.[23]

During the late seventies and early eighties, when oil prices rose after the 1973 war, extensive research was done to change coal to liquid hydrocarbons. However, coal-derived hydrocarbons were more expensive than crude oils. Another way to use coal is through gasification to a fuel gas mixture of CO and H_2 (medium Btu gas). This gas mixture could be used as a fuel or as a synthesis gas mixture for the production of fuels and chemicals via a Fischer Tropsch synthesis route. This process is

Table 1-6
Typical element analysis of some coals compared with a crude oil[23]

	Weight %					
	C	H	S	N	O	H/C mol 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

operative in South Africa for the production of hydrocarbon fuels. Fischer Tropsch synthesis is discussed in Chapter 4.

OIL SHALE

Oil shale is a low-permeable rock made of inorganic material interspersed with a high-molecular weight organic substance called "Kerogen." Heating the shale rock produces an oily substance with a complex structure.

The composition of oil shales differs greatly from one shale to another. For example, the amount of oil obtained from one ton of eastern U.S. shale deposit is only 10 gallons, compared to 30 gallons from western U.S. shale deposits.

Retorting is a process used to convert the shale to a high molecular-weight oily material. In this process, crushed shale is heated to high temperatures to pyrolyze Kerogen. The product oil is a viscous, high-molecular weight material. Further processing is required to change the oil into a liquid fuel.

Major obstacles to large-scale production are the disposal of the spent shale and the vast earth-moving operations. Table 1-7 is a typical analysis of a raw shale oil produced from retorting oil shale.

TAR SAND

Tar sands (oil sands) are large deposits of sand saturated with bitumen and water. Tar sand deposits are commonly found at or near the earth's surface entrapped in large sedimentary basins. Large accumulations of tar sand deposits are few. About 98% of all world tar sand is found in

Table 1-7
Typical analysis of shale oil

Test	Result
Gravity	19.7
Nitrogen, wt %	2.18
Conradson Carbon, wt %	4.5
Sulfur, wt %	0.74
Ash, wt %	0.06

seven large tar deposits. The oil sands resources in Western Canada sedimentary basin is the largest in the world. In 1997, it produced 99% of Canada's crude oil. It is estimated to hold 1.7–2.5 trillon barrels of bitumen in place. This makes it one of the largest hydrocarbon deposits in the world.[24] Tar sand deposits are covered by a semifloating mass of partially decayed vegetation approximately 6 meters thick.

Tar sand is difficult to handle. During summer, it is soft and sticky, and during the winter it changes to a hard, solid material.

Recovering the bitumen is not easy, and the deposits are either strip-mined if they are near the surface, or recovered in situ if they are in deeper beds. The bitumen could be extracted by using hot water and steam and adding some alkali to disperse it. The produced bitumen is a very thick material having a density of approximately 1.05 g/cm^3. It is then subjected to a cracking process to produce distillate fuels and coke. The distillates are hydrotreated to saturate olefinic components. Table 1-8 is a typical analysis of Athabasca bitumen.[25]

GAS HYDRATES

Gas hydrates are an ice-like material which is constituted of methane molecules encaged in a cluster of water molecules and held together by hydrogen bonds. This material occurs in large underground deposits found beneath the ocean floor on continental margins and in places north of the arctic circle such as Siberia. It is estimated that gas hydrate deposits contain twice as much carbon as all other fossil fuels on earth. This source, if proven feasible for recovery, could be a future energy as well as chemical source for petrochemicals.

Due to its physical nature (a solid material only under high pressure and low temperature), it cannot be processed by conventional methods used for natural gas and crude oils. One approach is by dissociating this

Table 1-8
Properties of Athabasca bitumen[25]

Gravity at 60°F (15.6°C)	6.0°API
UOP characterization factor	11.18
Pour point	+50°F (10°C)
Specific heat	0.35 cal/(g)(°C)
Calorific value	17,900 Btu/lb
Viscosity at 60°F (15.6°C)	3,000–300,000 poise
Carbon/hydrogen ratio	8.1
Components, %:	
asphaltenes	20.0
resins	25.0
oils	55.0
Ultimate analysis, %:	
carbon	83.6
hydrogen	10.3
sulfur	5.5
nitrogen	0.4
oxygen	0.2
Heavy metals. ppm:	
nickel	100
vanadium	250
copper	5

cluster into methane and water by injecting a warmer fluid such as sea water. Another approach is by drilling into the deposit. This reduces the pressure and frees methane from water. However, the environmental effects of such drilling must still be evaluated.[26]

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1. Hatch, L. F. and Matar, S., From Hydrocarbons to Petrochemicals, Gulf Publishing Company, 1981, p. 5.
2. “Gas Processing Handbook,” Hydrocarbon Processing, Vol. 69, No.4, 1990, p. 91.
3. Tuttle, R. and Allen, K., Oil and Gas Journal, Aug. 9, 1976, pp. 78–82.
4. “Gas Processing Handbook,” Hydrocarbon Processing, Vol. 69, No. 4, 1990, p. 77.

Coal

Oil Shale

Tar sand

Gas hydrate

Gas hydrate

Lecture (4)

Synthesis Gas

SYNTHESIS GAS

Synthesis gas generally refers to a mixture of carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide varies according to the type of feed, the method of production, and the end use of the gas.

During World War II, the Germans obtained synthesis gas by gasifying coal. The mixture was used for producing a liquid hydrocarbon mixture in the gasoline range using Fischer-Tropsch technology. Although this route was abandoned after the war due to the high production cost of these hydrocarbons, it is currently being used in South Africa, where coal is inexpensive (SASOL, II, and III).

There are different sources for obtaining synthesis gas. It can be produced by steam reforming or partial oxidation of any hydrocarbon ranging from natural gas (methane) to heavy petroleum residues. It can also

Table 4-1
Selected properties of carbon black from an oil furnace process

Analysis	General purpose	High abrasion	Conductive
Volatile matter wt %	0.9	1.6	1.6
pH	9.1	9.0	8.0
Average particle diameter, Å	550	280	190
Surface area, m^2/g (electron microscope method)	40	75	120
Surface area, m^2/g (nitrogen adsorption method)	25	75	220

be obtained by gasifying coal to a medium Btu gas (medium Btu gas consists of variable amounts of CO, CO_2, and H_2 and is used principally as a fuel gas). Figure 4-5 shows the different sources of synthesis gas.

A major route for producing synthesis gas is the steam reforming of natural gas over a promoted nickel catalyst at about 800°C:

$$CH_4(g) + H_2O(g) \; r \; CO(g) + 3H_2(g)$$

This route is used when natural gas is abundant and inexpensive, as it is in Saudi Arabia and the USA.

In Europe, synthesis gas is mainly produced by steam reforming naphtha. Because naphtha is a mixture of hydrocarbons ranging approximately from C_5-C_{10}, the steam reforming reaction may be represented using n-heptane:

$$CH_3(CH_2)_5CH_3 + 7H_2O(g) \; r \; 7CO(g) + 15H_2(g)$$

As the molecular weight of the hydrocarbon increases (lower H/C feed ratio), the H_2/CO product ratio decreases. The H_2/CO product ratio is approximately 3 for methane, 2.5 for ethane, 2.1 for heptane, and less than 2 for heavier hydrocarbons. Noncatalytic partial oxidation of hydrocarbons is also used to produce synthesis gas, but the H_2/CO ratio is lower than from steam reforming:

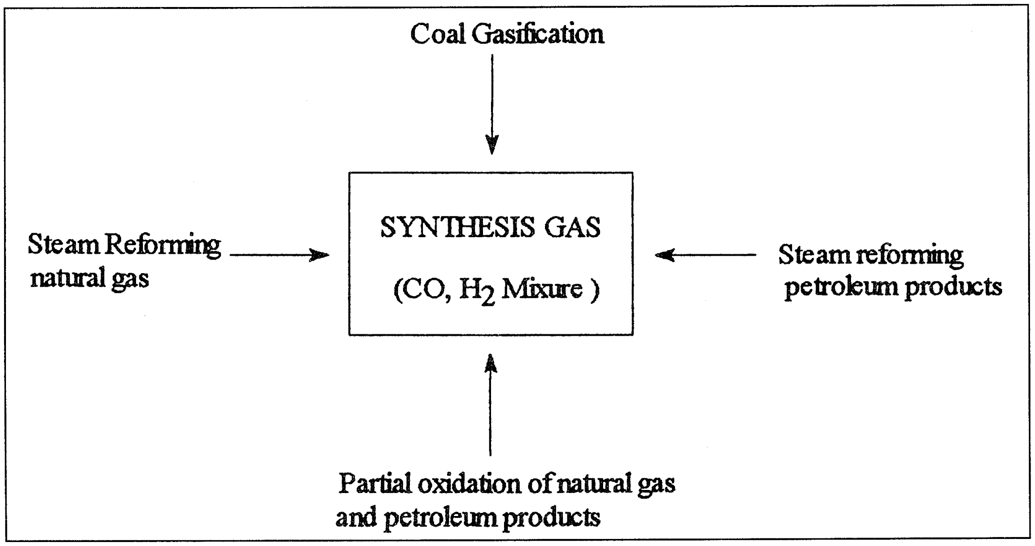


Figure 4-5. The different sources and routes to synthesis gas.

$$CH_4(g) + {}^1/_2O_2\ (g) \rightarrow CO\ (g) + 2H_2\ (g)$$

In practice, this ratio is even lower than what is shown by the stoichiometric equation because part of the methane is oxidized to carbon dioxide and water. When resids are partially oxidized by oxygen and steam at 1400–1450°C and 55–60 atmospheres, the gas consists of equal parts of hydrogen and carbon monoxide. Table 4-2 compares products from steam reforming natural gas with products from partial oxidation of heavy fuel oil.[14]

USES OF SYNTHESIS GAS

Synthesis gas is an important intermediate. The mixture of carbon monoxide and hydrogen is used for producing methanol. It is also used to synthesize a wide variety of hydrocarbons ranging from gases to naphtha to gas oil using Fischer Tropsch technology. This process may offer an alternative future route for obtaining olefins and chemicals. The hydroformylation reaction (Oxo synthesis) is based on the reaction of synthesis gas with olefins for the production of Oxo aldehydes and alcohols (Chapters 5, 7, and 8).

Synthesis gas is a major source of hydrogen, which is used for producing ammonia. Ammonia is the host of many chemicals such as urea, ammonium nitrate, and hydrazine. Carbon dioxide, a by-product from synthesis gas, reacts with ammonia to produce urea.

The production of synthesis gas from methane and the major chemicals based on it are noted in Chapter 5.

Hydrocarbons from Synthesis Gas (Fischer Tropsch Synthesis, FTS)

Most of the production of hydrocarbons by Fischer Tropsch method uses synthesis gas produced from sources that yield a relatively low

Table 4-2
Composition of synthesis gas from steam reforming natural gas and partial oxidation of fuel oil[14]

	Volume % dry sulfur free				
Process	CO	H_2	CO_2	N_2+A	CH_4
Steam reforming natural gas	15.5	75.7	8.1	0.2	0.5
Partial oxidation-heavy fuel oil	47.5	46.7	4.3	1.4	0.3

H_2/CO ratio, such as coal gasifiers. This, however, does not limit this process to low H_2/CO gas feeds. The only large-scale commercial process using this technology is in South Africa, where coal is an abundant energy source. The process of obtaining liquid hydrocarbons from coal through FTS is termed indirect coal liquefaction. It was originally intended for obtaining liquid hydrocarbons from solid fuels.[15] However, this method may well be applied in the future to the manufacture of chemicals through cracking the liquid products or by directing the reaction to produce more olefins.

The reactants in FTS are carbon monoxide and hydrogen. The reaction may be considered a hydrogenative oligomerization of carbon monoxide in presence of a heterogeneous catalyst.

The main reactions occurring in FTS are represented as:[16]

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \qquad \text{(olefins)}$$

$$(2n + 1)\ H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad \text{(paraffins)}$$

$$2nH_2 + nCO \rightarrow C_nH_{2n+2}\,O + (n\text{-}l)\ H_2O \qquad \text{(alcohols)}$$

The coproduct water reacts with carbon monoxide (the shift reaction), yielding hydrogen and carbon dioxide:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The gained hydrogen from the water shift reaction reduces the hydrogen demand for FTS. Water gas shift proceeds at about the same rate as the FT reaction. Studies of the overall water shift reaction in FT synthesis have been reviewed by Rofer Deporter.[17] Another side reaction also occurring in FTS reactors is the disproportionation of carbon monoxide to carbon dioxide and carbon:

$$2CO \rightarrow CO_2 + C$$

This reaction is responsible for the deposition of carbon in the reactor tubes in fixed-bed reactors and reducing heat transfer efficiency.

Fischer Tropsch synthesis is catalyzed by a variety of transition metals such as iron, nickel, and cobalt. Iron is the preferred catalyst due to its higher activity and lower cost. Nickel produces large amounts of methane, while cobalt has a lower reaction rate and lower selectivity than iron. By comparing cobalt and iron catalysts, it was found that cobalt promotes more middle-distillate products. In FTS, cobalt produces hydrocarbons plus water while iron catalyst produces hydrocarbons and carbon dioxide.[18] It appears that the iron catalyst promotes the shift reaction more than the cobalt catalyst. Dry[19] reviewed types of catalysts used in FT processes and their preparation.

Two reactor types are used commercially in FTS, a fixed bed and a fluid-bed. The fixed-bed reactors usually run at lower temperatures to avoid carbon deposition on the reactor tubes. Products from fixed-bed reactors are characterized by low olefin content, and they are generally heavier than products from fluid-beds. Heat distribution in fluid-beds, however, is better than fixed-bed reactors, and fluid-beds are generally operated at higher temperatures. Figure 4-6 shows the Synthol fluid-bed reactor.[20] Products are characterized by having more olefins, a high percent of light hydrocarbon gases, and lower molecular weight product slate than from fixed bed types. Table 4-3 compares the feed, the reaction conditions, and the products from the two reactor systems.

Fischer Tropsch technology is best exemplified by the SASOL projects in South Africa. After coal is gasified to a synthesis gas mixture, it is purified in a rectisol unit. The purified gas mixture is reacted in a synthol unit over an iron-based catalyst. The main products are gasoline, diesel fuel, and jet fuels. By-products are ethylene, propylene, alpha olefins, sulfur, phenol, and ammonia which are used for the production of downstream chemicals.[21]

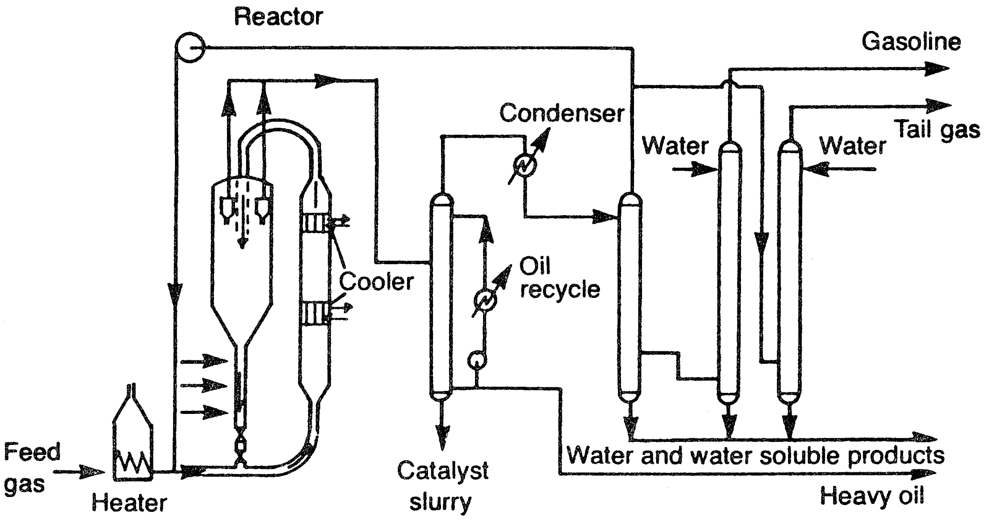


Figure 4-6. A flow chart of the Synthol process.[20]

Table 4-3
Typical analysis of products from Fischer-Tropsch fixed and fluid-bed reactors

Conditions	Fixed-Bed	Fluid-Bed
Temperature range °F	425–450	625–650
Conversion %	65	85
H_2/CO ratio	1.7	2.8
Products %		
Hydrocarbon Gases C_1-C_4	21.1	51.0
C_5-C_{12}	19.0	31.0
C_{13}-C_{18}	15.0	5.0
C_{19}-C_{31} (Heavy oil)	41.0	6.0
Oxygenates	3.9	7.0

A slurry bed reactor is in a pilot stage investigation. This type is characterized by having the catalyst in the form of a slurry. The feed gas mixture is bubbled through the catalyst suspension. Temperature control is easier than the other two reactor types. An added advantage to slurry-bed reactor is that it can accept a synthesis gas with a lower H_2/CO ratio than either the fixed-bed or the fluid-bed reactors.

Reactions occurring in FTS are essentially bond forming, and they release a large amount of heat. This requires an efficient heat removal system.

The FTS mechanism could be considered a simple polymerization reaction, the monomer being a C_1 species derived from carbon monoxide.[16] This polymerization follows an Anderson-Schulz-Flory distribution of molecular weights. This distribution gives a linear plot of the logarithm of yield of product (in moles) versus carbon number.[22] Under the assumptions of this model, the entire product distribution is determined by one parameter, α, the probability of the addition of a carbon atom to a chain (Figure 4-7).[16]

Much work has been undertaken to understand the steps and intermediates by which the reaction occurs on the heterogeneous catalyst surface. However, the exact mechanism is not fully established. One approach assumes a first-step adsorption of carbon monoxide on the catalyst surface followed by a transfer of an adsorbed hydrogen atom from an adjacent site to the metal carbonyl (M-CO):

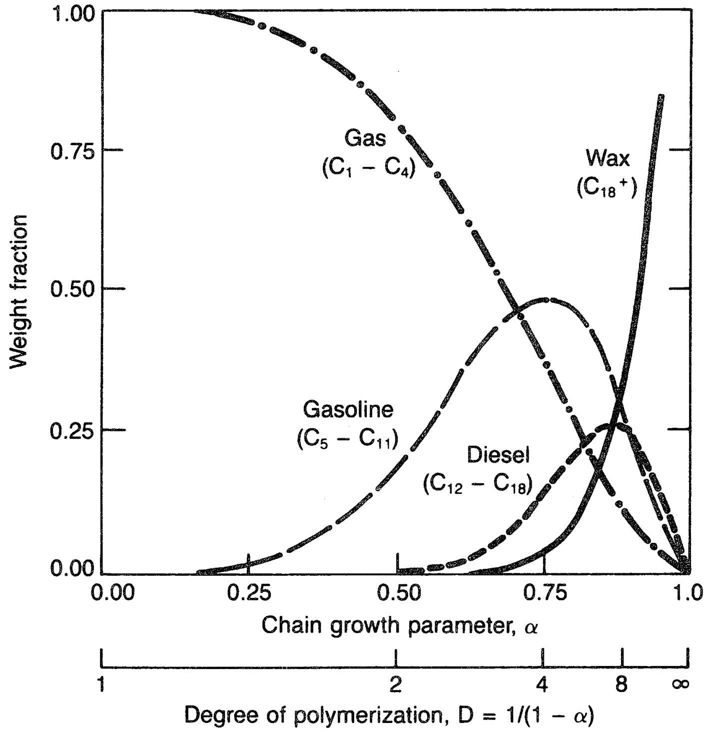
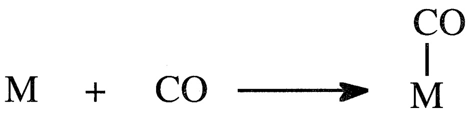
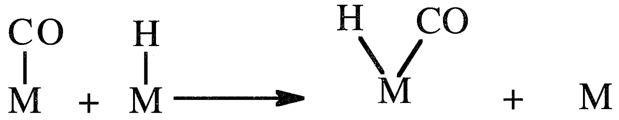


Figure 4-7. Yields of various products from FTS.[16]

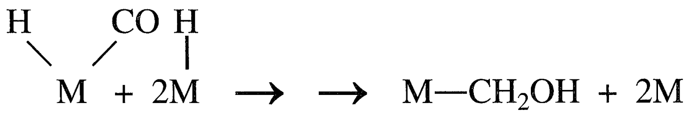


$$M + CO \longrightarrow \overset{CO}{\overset{|}{M}}$$

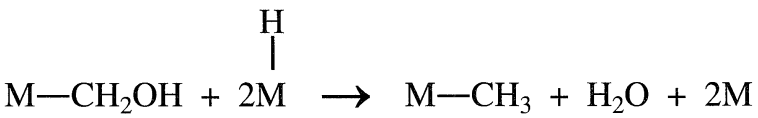


$$\overset{CO}{\overset{|}{M}} + \overset{H}{\overset{|}{M}} \longrightarrow \overset{H\quad CO}{\overset{\diagdown\ \diagup}{M}} + M$$

Note: M represents a catalyst surface adsorption site.
Successive hydrogenation produces a metal-methyl species accompanied by the release of water:

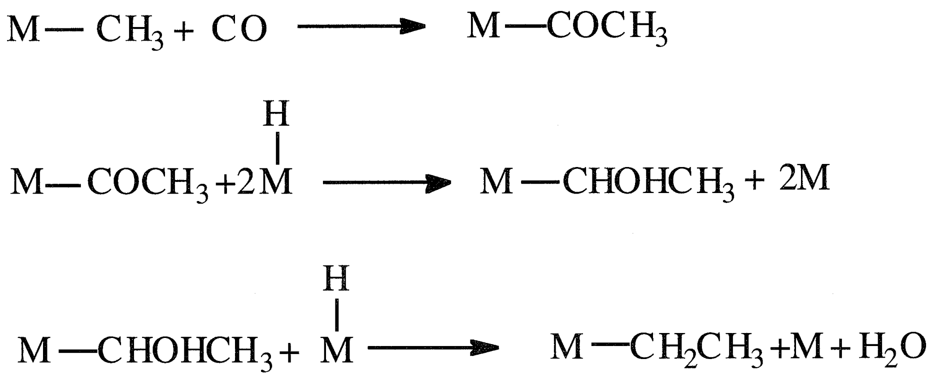


$$\overset{H\quad CO}{\overset{\diagdown\ \diagup}{M}} + 2\overset{H}{\overset{|}{M}} \longrightarrow \longrightarrow M\text{—}CH_2OH + 2M$$



$$M\text{—}CH_2OH + 2\overset{H}{\overset{|}{M}} \longrightarrow M\text{—}CH_3 + H_2O + 2M$$

In a subsequent step, the insertion of CO between the metal and the adsorbed methyl group occurs, followed by hydrogenation and elimination of water.

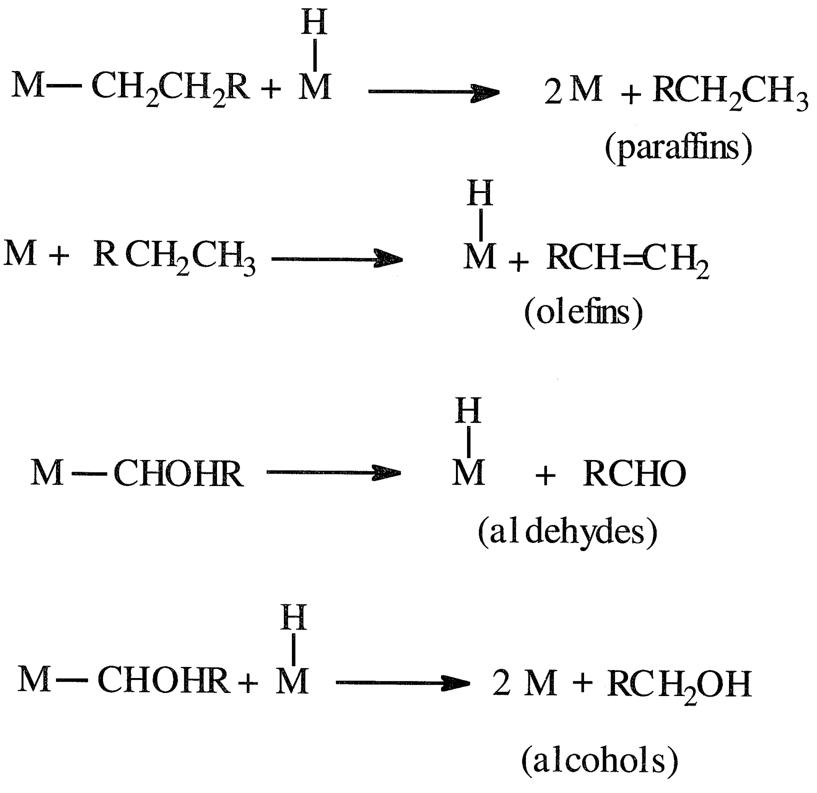


$$M{-}CH_3 + CO \longrightarrow M{-}COCH_3$$

$$M{-}COCH_3 + 2\overset{H}{\overset{|}{M}} \longrightarrow M{-}CHOHCH_3 + 2M$$

$$M{-}CHOHCH_3 + \overset{H}{\overset{|}{M}} \longrightarrow M{-}CH_2CH_3 + M + H_2O$$

The polymerization continues (as in the last three steps shown above) until termination occurs and the hydrocarbon is desorbed:



$$M{-}CH_2CH_2R + \overset{H}{\overset{|}{M}} \longrightarrow 2M + RCH_2CH_3$$

(paraffins)

$$M + RCH_2CH_3 \longrightarrow \overset{H}{\overset{|}{M}} + RCH{=}CH_2$$

(olefins)

$$M{-}CHOHR \longrightarrow \overset{H}{\overset{|}{M}} + RCHO$$

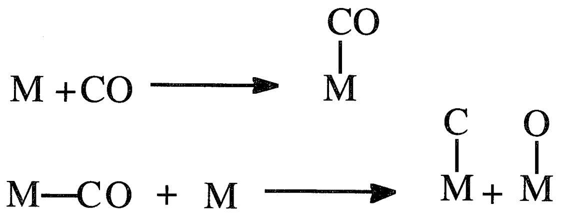
(aldehydes)

$$M{-}CHOHR + \overset{H}{\overset{|}{M}} \longrightarrow 2M + RCH_2OH$$

(alcohols)

The last two steps shown above explain the presence of oxygenates in FTS products.

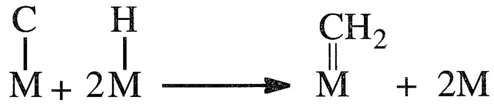
Alternatively, an intermediate formation of an adsorbed methylene on the catalyst surface through the dissociative adsorption of carbon monoxide has been considered:



$$\mathrm{M + CO \longrightarrow \overset{CO}{\overset{|}{M}}}$$

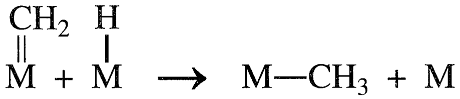
$$\mathrm{M{-}CO + M \longrightarrow \overset{C}{\overset{|}{M}} + \overset{O}{\overset{|}{M}}}$$

The formed metal carbide (M-C) is then hydrogenated to a reactive methylene metal species.



$$\mathrm{\overset{C}{\overset{|}{M}} + 2\overset{H}{\overset{|}{M}} \longrightarrow \overset{CH_2}{\overset{\|}{M}} + 2M}$$

The methylene intermediate abstracts a hydrogen and is converted to an adsorbed methyl. Reaction of the methyl with the methylene produces an ethyl-metal species. Successive reactions of the methylene with the formed ethyl produces a long chain adsorbed alkyl.

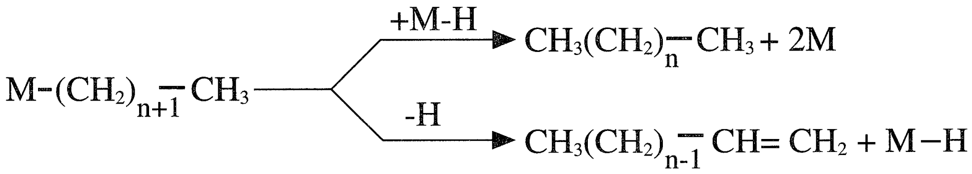


$$\mathrm{\overset{CH_2}{\overset{\|}{M}} + \overset{H}{\overset{|}{M}} \longrightarrow M{-}CH_3 + M}$$

$$\mathrm{M{=}CH_2 + M{-}CH_3 \longrightarrow M{-}CH_2{-}CH_3 + M}$$

$$\mathrm{M{-}CH_2{-}CH_3 + nM{=}CH_2 \longrightarrow M{-}(CH_2)_{n+1}{-}CH_3 + nM}$$

The adsorbed alkyl species can either terminate to a paraffin by a hydrogenation step or to an olefin by a dehydrogenation step:



$$\mathrm{M{-}(CH_2)_{n+1}{-}CH_3 \xrightarrow{+M{-}H} CH_3(CH_2)_n{-}CH_3 + 2M}$$

$$\mathrm{M{-}(CH_2)_{n+1}{-}CH_3 \xrightarrow{-H} CH_3(CH_2)_{n-1}{-}CH{=}CH_2 + M{-}H}$$

The carbide mechanism, however, does not explain the formation of oxygenates in FTS products.[23]

Synthetic gas(syn gas): H2+CO

Importance:

1-Raw material and basic for production of a lot of

Materials such as methanol.

2-Used in process where H_2 is required.

Syn gas production:

1940:from coal C + H_2O $\rightarrow CO+H_2$

Coke steam

Now: from petroleum fraction or natural gas

HCs feed:1-NG 2-Pet.fraction

Syn.gas:$CO+H_2$ IF H_2 is required only $CO \rightarrow CO_2$

Source of H_2:

1-Cata.reforming 80-85%

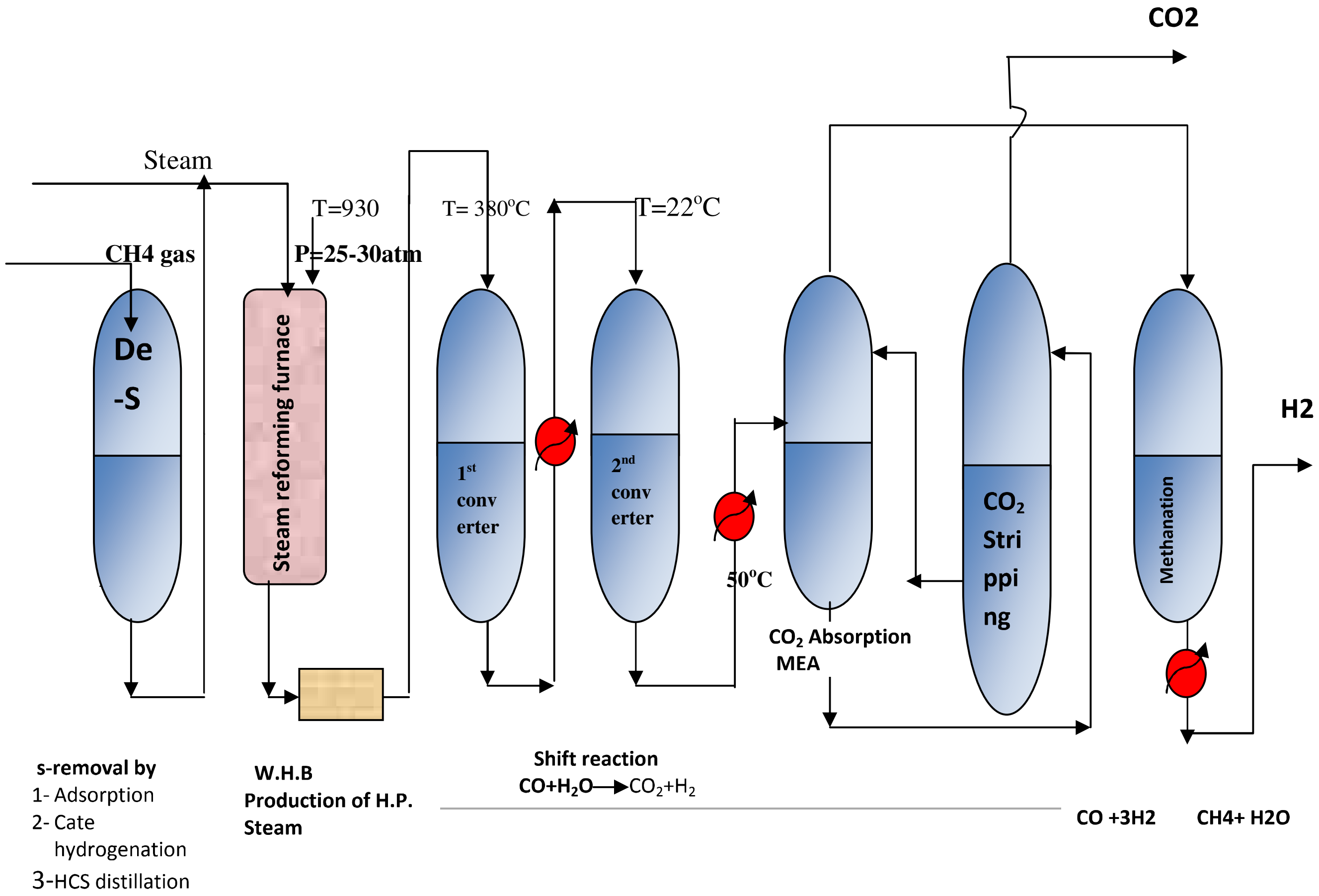
2-Cata. Cracking 60-80%

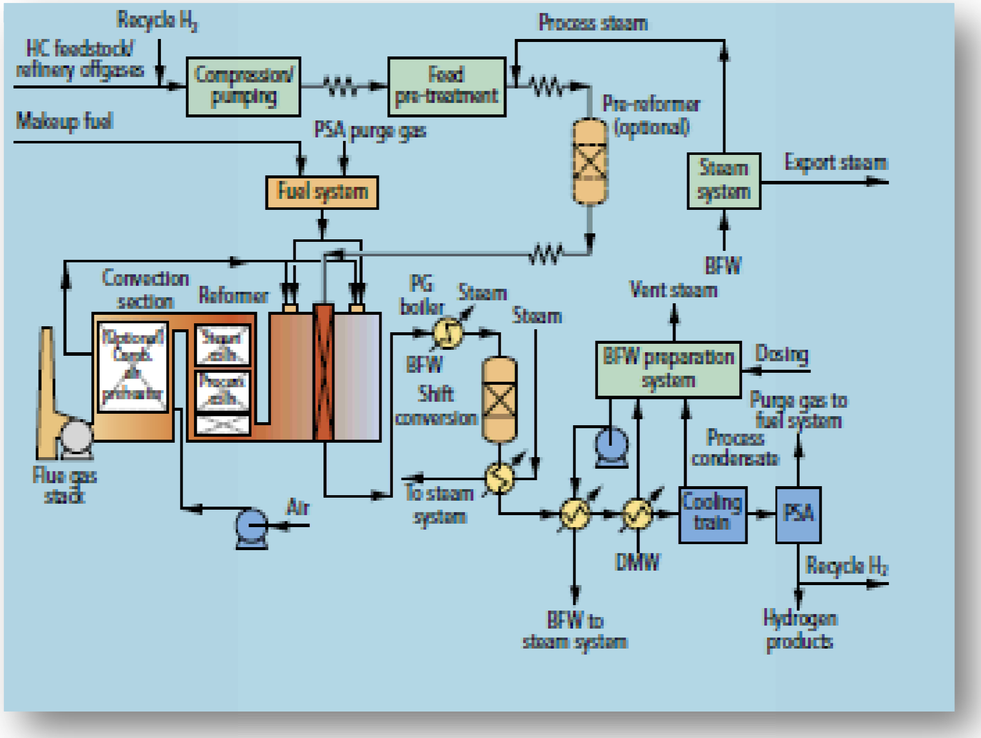
3-Dehydrogentation 90%

4-Electrolysis of water high purity 1m3 required 4940 Kw of electricity.

Hydrogen production from HCs feed

Hydrogen by steam reforming





Application: Production of hydrogen (H_2) from hydrocarbon (HC) feed stocks by steam reforming.

Feed stocks: Ranging from natural gas to heavy naphtha as well as potential refinery off gases. Many recent refinery hydrogen plants have multiple feedstock flexibility, either in terms of backup or alternative or mixed feed. Automatic feedstock change-over has also successfully been applied by Technip in several modern plants with multiple feed stock flexibility.

Description: The generic flow sheet consists of feed pre-treatment, pre reforming (optional), steam-HC reforming, shift conversion and hydrogen purification by pressure swing adsorption (PSA). However, it is often tailored to satisfy specific requirements. Feed pre-treatment normally involves removal of sulfur, chlorine andother catalyst poisons after preheating to 350 – 400°C. The treated feed gas mixed with process steam is reformed in a fired reformer (with adiabatic pre-reformer upstream, if used) after necessary super-heating. The net reforming reactions are strongly endothermic. Heat is supplied by combusting PSA purge gas, supplemented by makeup fuel in multiple burners in a top-fired furnace.

Reforming severity is optimized for each specific case. Waste heat from reformed gas is recovered through steam generation before the water-gas shift conversion. Most of the carbon monoxide (CO) is further converted to hydrogen. Process condensate resulting from heat recovery and cooling is separated and generally reused in the steam system after necessary treatment. The entire steam generation is usually on natural circulation, which adds to higher reliability. The gas flows to the PSA unit that provides high-purity hydrogen product (up to < 1 ppm CO) at neart inlet pressures. Typical specific energy consumption based on feed + fuel – export steam ranges between 3 Gcal/KNm3 and 3.5 Gcal/KNm3 (330 – 370 Btu/ scf) LHV, depending upon the feedstock, plant capacity, optimization criteria and steam export requirements. Recent advances include integration of hydrogen recovery and generation and recuperative (post-) reforming, also for capacity retrofits.

Commercial plants: Technip has been involved in over 240 hydrogen plants worldwide.

Reactions:

1-$CH_4+H_2O \rightarrow CO+3H_2$

2-$CO+H_2O \rightarrow CO2+H_2$ Shift reaction.

3-$CO+3H_2 \rightarrow CH_4+H_2O$ Methanation.

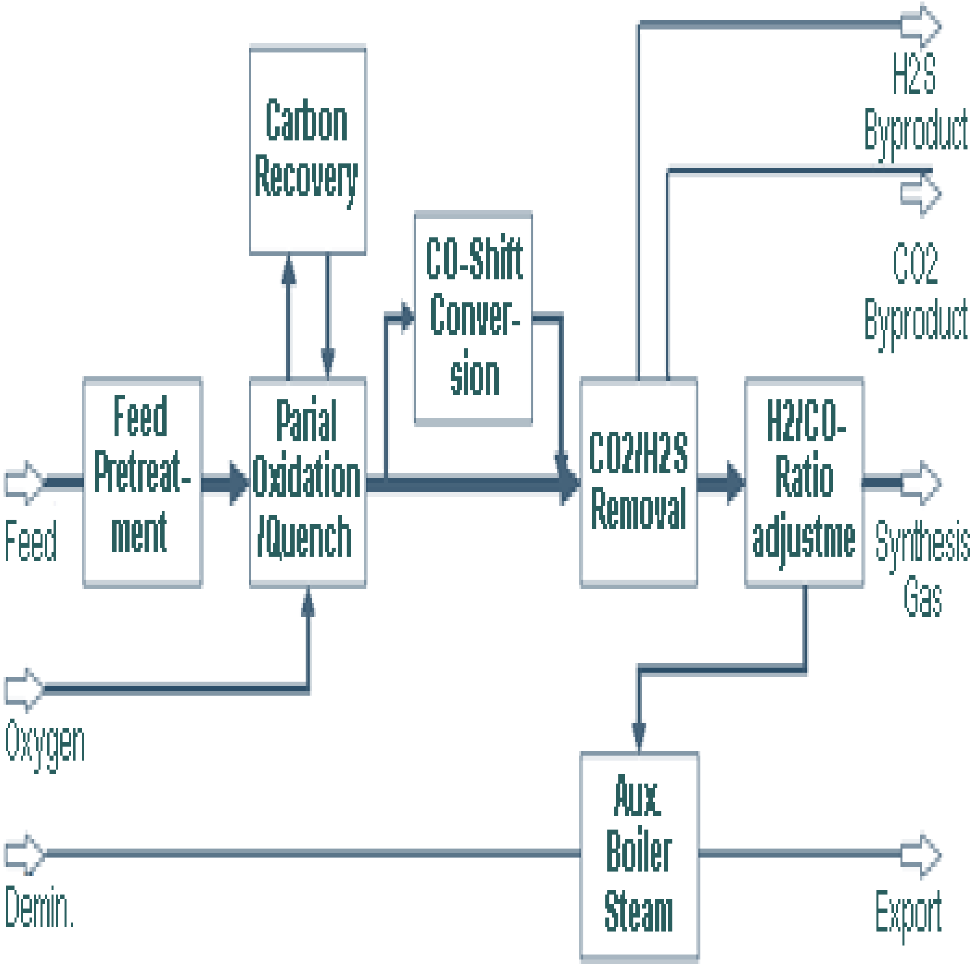
Operating conditions:

$T=800\text{-}900^{O}C$ P=25-30 atm. Cata.=Ni(SRF)

H_2O/C high ratio

Partial oxidation

Partial oxidation (**POX**) is a type of chemical reaction. It occurs when a substoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich syngas which can then be put to further use, for example in a fuel cell.



PO:Advantages:

1-Flexibility of use of HCs fuel,pet.fraction,crude oil with high sulfer content and residue.

2-It is used when NG or light fractions is not aviliable or when its prices are high.

3- Dose need catalyst.

4-Need of oxygen unit to produce oxygen.

Reactions:

$CH_4+O_2 \rightarrow CO_2+H_2O$

$CH_4+CO_2 \rightarrow 2CO+2H_2$

$CH_4+H_2O \rightarrow CO+3H_2$

Basic steps:

1-Gasification:

a- process occur in reactor lined with fire bricks without cata.

b-reaction occur between primary heated feed with oxygen,steam and it is supplied through burners.

c-T=1300-1500°C P=Higher than 10 atm.(40-90 atm.)

2-Cooling: Two types according to companies:

a-Quench system:Texco process .

b- W.H.B.:Shell process.

3-Removal of soot. 4-**Conversion of CO to CO_2** 5-**Removal of CO_2,H_2S.**

4- Removal of inert gases like Ar,CO.

5- Compression of resultant gases(H_2) or mixture(CO,H_2)

Comprism between Steam reforming(SR)and Parital oxidation(PO)

Properties	SR	PO
Feed	More important when CH_4 or NG as feed	Used for heavy pet. Fraction and residue
Cata.	Need Cata.	Does not need Cata
Economic	More economic due to low investment cost, also no need to oxygen unit	Less economic due to high investment cost, and the demand of oxygen unit.

Lecture (5)

Olefinic Hydrocarbons

OLEFINIC HYDROCARBONS

The most important olefins used for the production of petrochemicals are ethylene, propylene, the butylenes, and isoprene. These olefins are usually coproduced with ethylene by steam cracking ethane, LPG, liquid petroleum fractions, and residues. Olefins are characterized by their higher reactivities compared to paraffinic hydrocarbons. They can easily react with inexpensive reagents such as water, oxygen, hydrochloric acid, and chlorine to form valuable chemicals. Olefins can even add to themselves to produce important polymers such as polyethylene and polypropylene. Ethylene is the most important olefin for producing petrochemicals, and therefore, many sources have been sought for its production. The following discusses briefly, the properties of these olefinic intermediates.

ETHYLENE ($CH_2{=}CH_2$)

Ethylene (ethene), the first member of the alkenes, is a colorless gas with a sweet odor. It is slightly soluble in water and alcohol. It is a highly active compound that reacts easily by addition to many chemical reagents. For example, ethylene with water forms ethyl alcohol. Addition of chlorine to ethylene produces ethylene dichloride (1,2-dichloroethane), which is cracked to vinyl chloride. Vinyl chloride is an important plastic precursor. Ethylene is also an active alkylating agent. Alkylation of benzene with ethylene produces ethyl benzene, which is dehydrogenated to styrene. Styrene is a monomer used in the manufacture of many commercial polymers and copolymers. Ethylene can be polymerized to different grades of polyethylenes or copolymerized with other olefins.

Catalytic oxidation of ethylene produces ethylene oxide, which is hydrolyzed to ethylene glycol. Ethylene glycol is a monomer for the production of synthetic fibers. Chapter 7 discusses chemicals based on ethylene, and Chapter 12 covers polymers and copolymers of ethylene.

Ethylene is a constituent of refinery gases, especially those produced from catalytic cracking units. The main source for ethylene is the steam cracking of hydrocarbons (Chapter 3). Table 2-2 shows the world ethylene production by source until the year 2000.[4] U.S. production of ethylene was approximately 51 billion lbs in 1997.[5]

PROPYLENE ($CH_3CH{=}CH_2$)

Like ethylene, propylene (propene) is a reactive alkene that can be obtained from refinery gas streams, especially those from cracking processes. The main source of propylene, however, is steam cracking of hydrocarbons, where it is coproduced with ethylene. There is no special process for propylene production except the dehydrogenation of propane.

$$CH_3CH_2{-}CH_3 \xrightarrow{\text{Catalyst}} CH_3CH{=}CH_2 + H_2$$

Table 2-2
World ethylene production by feedstock[4] (MMtpd)

Feedstock	1990	1995	2000
Ethane/refinery gas	16	18	20
LPG	6	9	12
Naphtha/condensates	30	36	40
Gasoil/others	4	5	6
Total	56	68	78

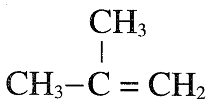
Propylene can be polymerized alone or copolymerized with other monomers such as ethylene. Many important chemicals are based on propylene such as isopropanol, allyl alcohol, glycerol, and acrylonitrile.

BUTYLENES (C_4H_8)

Butylenes (butenes) are by-products of refinery cracking processes and steam cracking units for ethylene production.

Dehydrogenation of butanes is a second source of butenes. However, this source is becoming more important because isobutylene (a butene isomer) is currently highly demanded for the production of oxygenates as gasoline additives.

There are four butene isomers: three unbranched, "normal" butenes (n-butenes) and a branched isobutene (2-methylpropene). The three n-butenes are 1-butene and cis- and trans- 2-butene. The following shows the four butylene isomers:

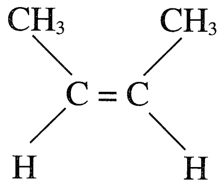


$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

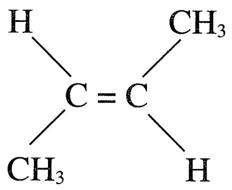
Isobutene

$CH_2=CHCH_2CH_3$

1- Butene



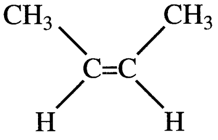
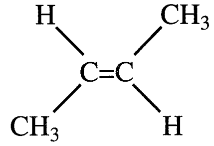
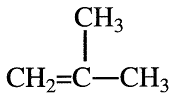
cis-2- Butene



trans-2-Butene

The industrial reactions involving cis- and trans-2-butene are the same and produce the same products. There are also addition reactions where both 1-butene and 2-butene give the same product. For this reason, it is economically feasible to isomerize 1-butene to 2-butene (cis and trans) and then separate the mixture. The isomerization reaction yields two streams, one of 2-butene and the other of isobutene, which are separated by fractional distillation, each with a purity of 80–90%. Table 2-3[6] shows the boiling points of the different butene isomers.

Table 2-3
Structure and boiling points of C_4 olefins[6]

Name	Structure	Boiling Point°C
1-Butene	$CH_2=CHCH_2CH_3$	–6.3
cis-2-Butene		+3.7
trans-2-Butene		+0.9
Isobutene	 $CH_2=C(CH_3)-CH_3$	–6.6

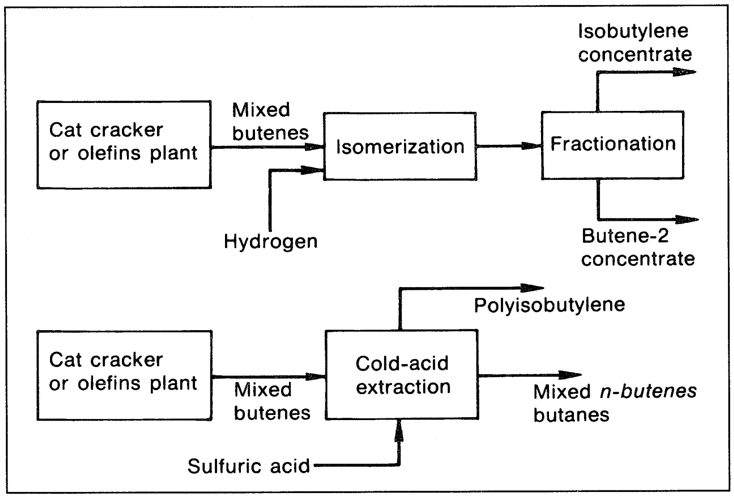


Figure 2-1. The two processes for separating n-butenes and isobutylene.[7]

An alternative method for separating the butenes is by extracting isobutene (due to its higher reactivity) in cold sulfuric acid, which polymerizes it to di- and triisobutylene. The dimer and trimer of isobutene have high octane ratings and are added to the gasoline pool.

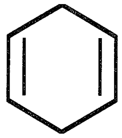
Figure 2-1 shows the two processes for the separation of n-butenes from isobutene.[7]

THE DIENES

Dienes are aliphatic compounds having two double bonds. When the double bonds are separated by only one single bond, the compound is a conjugated diene (conjugated diolefin). Nonconjugated diolefins have the double bonds separated (isolated) by more than one single bond. This latter class is of little industrial importance. Each double bond in the compound behaves independently and reacts as if the other is not present.[8] Examples of nonconjugated dienes are 1,4-pentadiene and 1,4-cyclo-hexadiene. Examples of conjugated dienes are 1,3-butadiene and 1,3-cyclohexadiene.

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

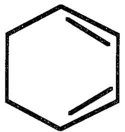
1,4-Pentadiene



1,4-Cyclohexadiene

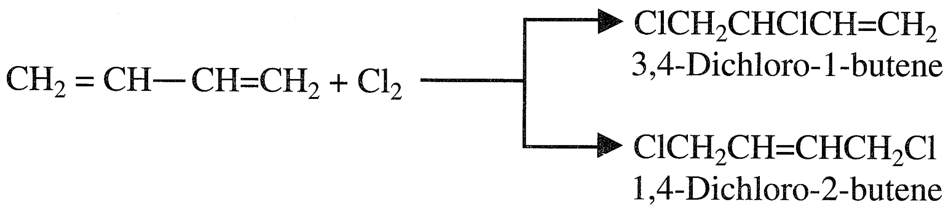
$CH_2{=}CH{-}CH{=}CH_2$

1,3-Butadiene



1,3-Cyclohexadiene

An important difference between conjugated and nonconjugated dienes is that the former compounds can react with reagents such as chlorine, yielding 1,2- and 1,4-addition products. For example, the reaction between chlorine and 1,3-butadiene produces a mixture of 1,4-dichloro-2-butene and 3,4-dichloro- 1-butene:



$CH_2{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow ClCH_2CHClCH{=}CH_2$

3,4-Dichloro-1-butene

$CH_2{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow ClCH_2CH{=}CHCH_2Cl$

1,4-Dichloro-2-butene

When polymerizing dienes for synthetic rubber production, coordination catalysts are used to direct the reaction to yield predominantly 1,4-addition polymers. Chapter 11 discusses addition polymerization. The following reviews some of the physical and chemical properties of butadiene and isoprene.

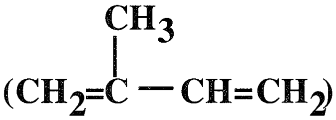
BUTADIENE ($CH_2{=}CH{-}CH{=}CH_2$)

Butadiene is by far the most important monomer for synthetic rubber production. It can be polymerized to polybutadiene or copolymerized with styrene to styrene-butadiene rubber (SBR). Butadiene is an important intermediate for the synthesis of many chemicals such as hexamethylenediamine and adipic acid. Both are monomers for producing nylon. Chloroprene is another butadiene derivative for the synthesis of neoprene rubber.

The unique role of butadiene among other conjugated diolefins lies in its high reactivity as well as its low cost.

Butadiene is obtained mainly as a coproduct with other light olefins from steam cracking units for ethylene production. Other sources of butadiene are the catalytic dehydrogenation of butanes and butenes, and dehydration of 1,4-butanediol. Butadiene is a colorless gas with a mild aromatic odor. Its specific gravity is 0.6211 at 20°C and its boiling temperature is –4.4°C. The U.S. production of butadiene reached 4.1 billion pounds in 1997 and it was the 36th highest-volume chemical.[5]

Isoprene



$$(CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2)$$

Isoprene (2-methyl-1,3-butadiene) is a colorless liquid, soluble in alcohol but not in water. Its boiling temperature is 34.1°C.

Isoprene is the second important conjugated diene for synthetic rubber production. The main source for isoprene is the dehydrogenation of C_5 olefins (tertiary amylenes) obtained by the extraction of a C_5 fraction from catalytic cracking units. It can also be produced through several synthetic routes using reactive chemicals such as isobutene, formaldehyde, and propene (Chapter 3).

The main use of isoprene is the production of polyisoprene. It is also a comonomer with isobutene for butyl rubber production.

AROMATIC HYDROCARBONS

Benzene, toluene, xylenes (BTX), and ethylbenzene are the aromatic hydrocarbons with a widespread use as petrochemicals. They are important precursors for many commercial chemicals and polymers such as phenol, trinitrotoluene (TNT), nylons, and plastics. Aromatic compounds are characterized by having a stable ring structure due to the overlap of the π-orbitals (resonance).

Accordingly, they do not easily add to reagents such as halogens and acids as do alkenes. Aromatic hydrocarbons are susceptible, however, to electrophilic substitution reactions in presence of a catalyst.

Aromatic hydrocarbons are generally nonpolar. They are not soluble in water, but they dissolve in organic solvents such as hexane, diethyl ether, and carbon tetrachloride.

EXTRACTION OF AROMATICS

Benzene, toluene, xylenes (BTX), and ethylbenzene are obtained mainly from the catalytic reforming of heavy naphtha. The product reformate is rich in C_6, C_7, and C_8 aromatics, which could be extracted by a suitable solvent such as sulfolane or ethylene glycol.

These solvents are characterized by a high affinity for aromatics, good thermal stability, and rapid phase separation. The Tetra extraction process by Union Carbide (Figure 2-2) uses tetraethylene glycol as a solvent.[9] The feed (reformate), which contains a mixture of aromatics, paraffins,

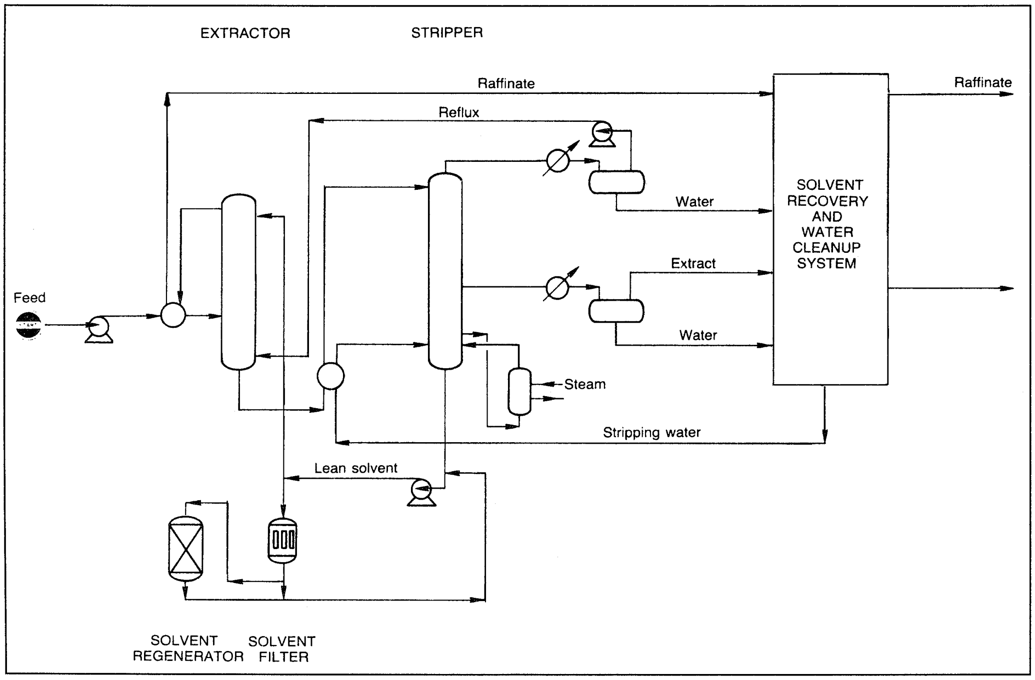


Figure 2-2. The Union Carbide aromatics extraction process using tetraethylene glycol.[9]

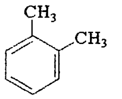
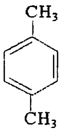
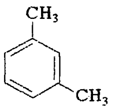
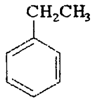
and naphthenes, after heat exchange with hot raffinate, is countercurrently contacted with an aqueous tetraethylene lycol solution in the extraction column. The hot, rich solvent containing BTX aromatics is cooled and introduced into the top of a stripper column. The aromatics extract is then purified by extractive distillation and recovered from the solvent by steam stripping. Extractive distillation has been reviewed by Gentry and Kumar.[10] The raffinate (constituted mainly of paraffins, isoparaffins and cycloparaffins) is washed with water to recover traces of solvent and then sent to storage. The solvent is recycled to the extraction tower.

The extract, which is composed of BTX and ethylbenzene, is then fractionated. Benzene and toluene are recovered separately, and ethylbenzene and xylenes are obtained as a mixture (C_8 aromatics).

Due to the narrow range of the boiling points of C_8 aromatics (Table 2-4), separation by fractional distillation is difficult. A superfractionation technique is used to segregate ethylbenzene from the xylene mixture.

Because p-xylene is the most valuable isomer for producing synthetic fibers, it is usually recovered from the xylene mixture. Fractional crystallization used to be the method for separating the isomers, but the yield was only 60%. Currently, industry uses continuous liquid-phase adsorption separation processes.[11] The overall yield of p-xylene is increased

Table 2-4
Boiling and freezing points of C_8 aromatics

Name	Structure	Boiling point °C	Freezing point °C
o-Xylene		144.4	–25.2
p-Xylene		138.4	+13.3
m-Xylene		139.1	–46.8
Ethylbenzene		136.2	–94.9

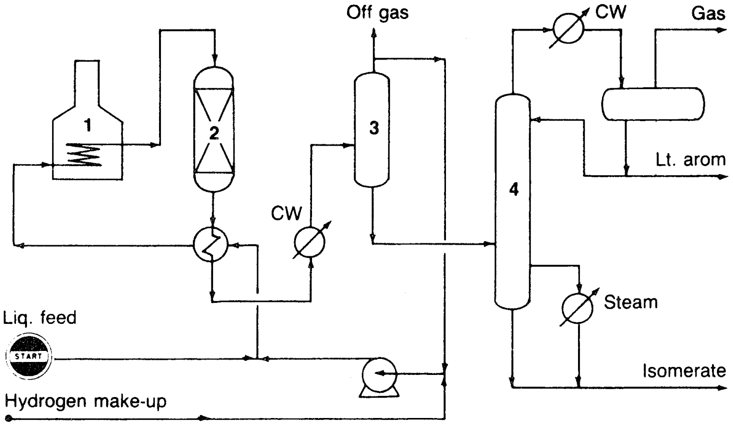


Figure 2-3. Flow diagram of the Mobil xylene isomerization process.[12]

by incorporating an isomerization unit to isomerize o- and m-xylenes to p-xylene. An overall yield of 90% p-xylene could be achieved. Figure 2-3 is a flow diagram of the Mobil isomerization process. In this process, partial conversion of ethylbenzene to benzene also occurs. The catalyst used is shape selective and contains ZSM-5 zeolite.[12]

Lecture 6

Chemicals Based on Benzene, Toluene, and Xylenes

INTRODUCTION

The primary sources of benzene, toluene, and xylenes (BTX) are refinery streams, especially from catalytic reforming and cracking, and pyrolysis gasoline from steam cracking and from coal liquids. BTX and ethyl benzene are extracted from these streams using selective solvents such as sulfolene or ethylene glycol. The extracted components are separated through lengthy fractional distillation, crystallization, and isomerization processes (Chapter 2).

The reactivity of C_6, C_7, C_8 aromatics is mainly associated with the benzene ring. Aromatic compounds in general are liable for electrophilic substitution. Most of the chemicals produced directly from benzene are obtained from its reactions with electrophilic reagents. Benzene could be alkylated, nitrated, or chlorinated to important chemicals that are precursors for many commercial products.

Toluene and xylenes (methylbenzenes) are substituted benzenes. Although the presence of methyl substituents activates the benzene ring for electrophilic attack, the chemistry of methyl benzenes for producing commercial products is more related to reactions with the methyl than with the phenyl group. As an electron-withdrawing substituent (of methane), the phenyl group influences the methyl hydrogens and makes them more available for chemical attack. The methyl group could be easily oxidized or chlorinated as a result of the presence of the phenyl substituent.

REACTIONS AND CHEMICALS OF BENZENE

Benzene (C_6H_6) is the most important aromatic hydrocarbon. It is the precursor for many chemicals that may be used as end products or intermediates. Almost all compounds derived directly from benzene are converted to other chemicals and polymers. For example, hydrogenation of benzene produces cyclohexane. Oxidation of cyclohexane produces cyclohexanone, which is used to make caprolactam for nylon manufacture. Due to the resonance stabilization of the benzene ring, it is not easily polymerized. However, products derived from benzene such as styrene, phenol, and maleic anhydride can polymerize to important commercial products due to the presence of reactive functional groups. Benzene could be alkylated by different alkylating agents, hydrogenated to cyclohexane, nitrated, or chlorinated.

The current world benzene capacity is approximately 35 million tons. The 1994 U.S. production of benzene was about 14.7 million pounds.[1]

The chemistry for producing the various chemicals from benzene is discussed in this section. Figure 10-1 shows the important chemicals derived from benzene.

ALKYLATION OF BENZENE

Benzene can be alkylated in the presence of a Lewis or a Bronsted acid catalyst. Olefins such as ethylene, propylene, and C_{12}–C_{14} alpha olefins are used to produce benzene alkylates, which have great commercial value. Alkyl halides such as monochloroparaffins in the C_{12}–C_{14} range also serve this purpose.

The first step in alkylation is the generation of a carbocation (carbonium ion). When an olefin is the alkylating agent, a carbocation intermediate forms.

$$RCH{=}CH_2 \xrightarrow{H^+} [R\overset{+}{C}HCH_3]$$

Carboncations also form from an alkyl halide when a Lewis acid catalyst is used. Aluminum chloride is the commonly used Friedel-Crafts alkylation catalyst. Friedel-Crafts alkylation reactions have been reviewed by Roberts and Khalaf:[2]

$$RCl + AlCl_3 \rightarrow [R^+ \_\_\_\_ AlCl_4^-]$$

The next step is an attack by the carbocation on the benzene ring, followed by the elimination of a proton and the formation of a benzene alkylate:

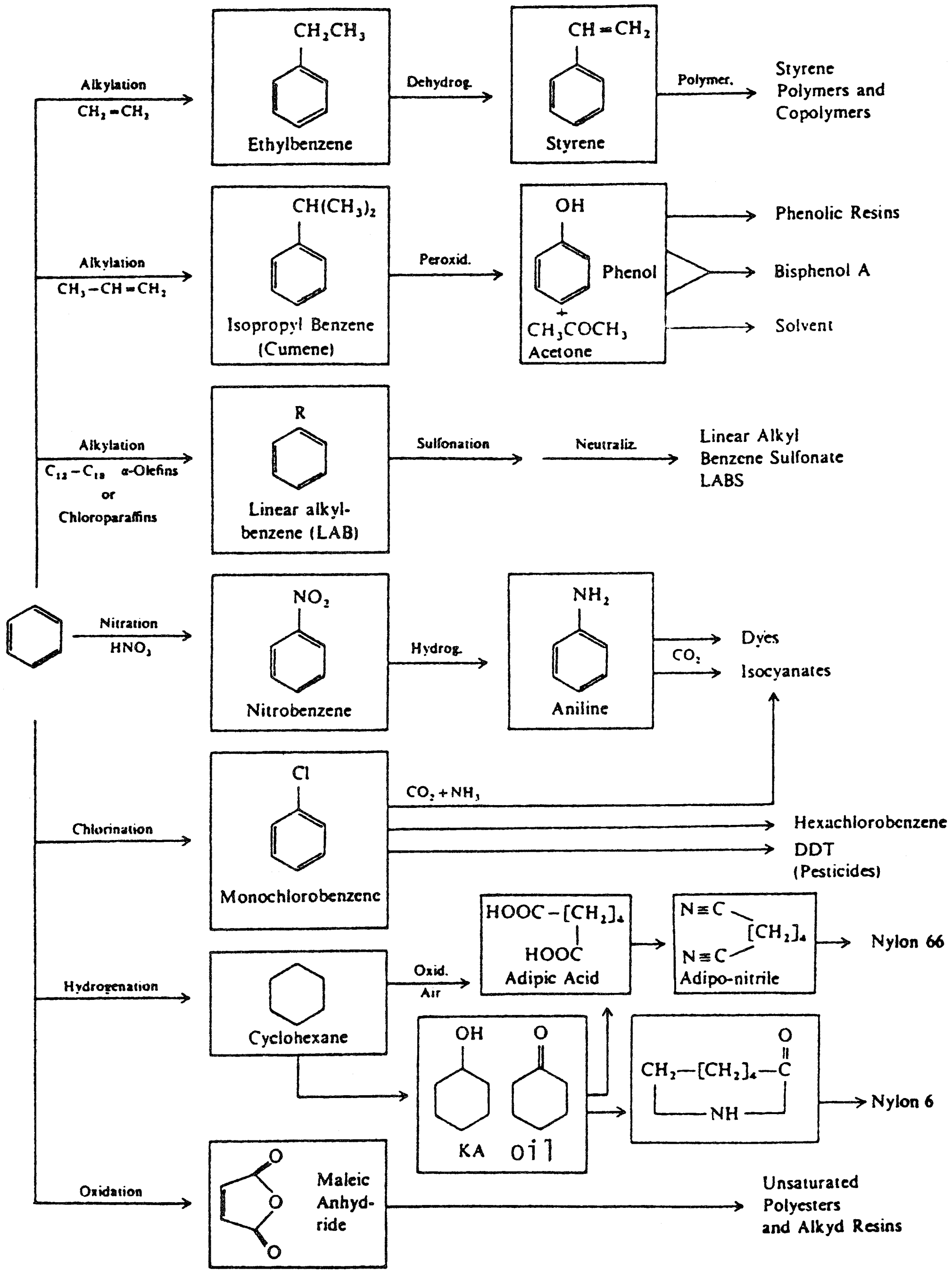
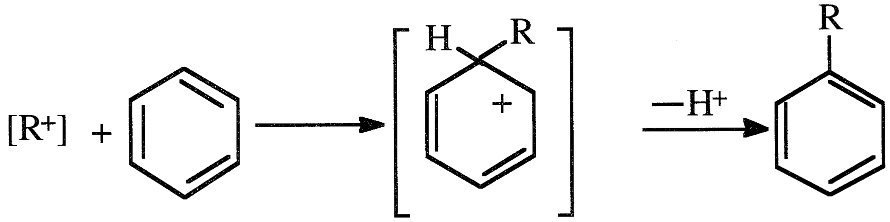
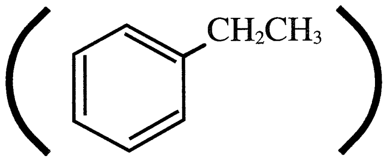


Figure 10-1. Important chemicals based on benzene.

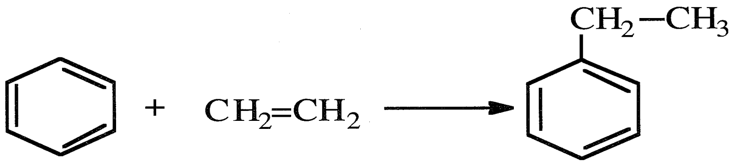


Ethylbenzene



Ethylbenzene (EB) is a colorless aromatic liquid with a boiling point of 136.2°C, very close to that of *p*-xylene. This complicates separating it from the C_8 aromatic equilibrium mixture obtained from catalytic reforming processes. (See Chapter 2 for separation of C_8 aromatics). Ethylbenzene obtained from this source, however, is small compared to the synthetic route.

The main process for producing EB is the catalyzed alkylation of benzene with ethylene:



Many different catalysts are available for this reaction. $AlCl_3$-HCl is commonly used. Ethyl chloride may be substituted for HCl in a mole-for-mole basis. Typical reaction conditions for the liquid-phase $AlCl_3$ catalyzed process are 40–100°C and 2–8 atmospheres. Diethylbenzene and higher alkylated benzenes also form. They are recycled and dealkylated to EB.

The vapor-phase Badger process (Figure 10-2), which has been commercialized since 1980, can accept dilute ethylene streams such as those produced from FCC off gas.[3] A zeolite type heterogeneous catalyst is used in a fixed bed process. The reaction conditions are 420°C and 200–300 psi. Over 98% yield is obtained at 90% conversion.[4,5] Polyethylbenzene (polyalkylated) and unreacted benzene are recycled and join the fresh feed to the reactor. The reactor effluent is fed to the benzene fractionation system to recover unreacted benzene. The bottoms

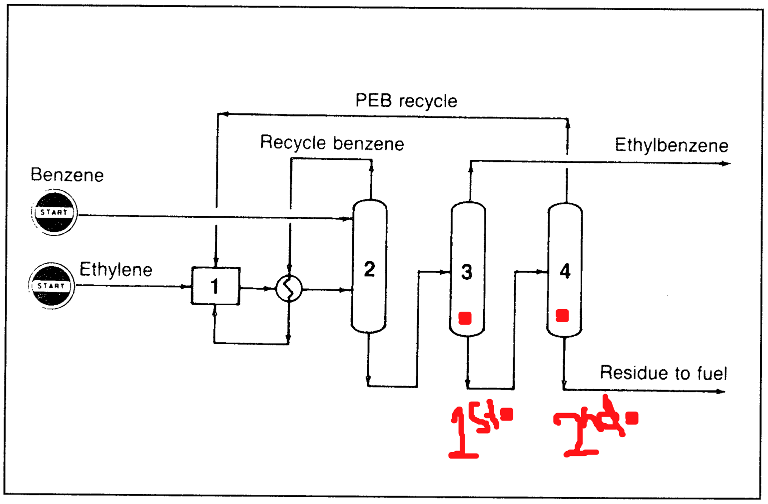
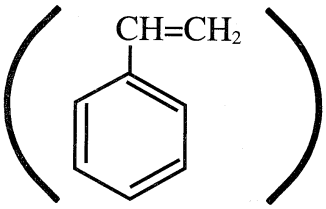


Figure 10-2. The Badger process for producing ethylbenzene:[3] (1) reactor, (2) fractionator (for recovery of unreacted benzene), (3) EB fractionator, (4) polyethylbenzene recovery column.

containing ethylbenzene and heavier polyalkylates are fractionated in two columns. The first column separates the ethylbenzene product, and the other separates polyethylbenzene for recycling. An optimization study of EB plants by constraint control was conducted by Hummel et al. They concluded that optimum operation could be maintained through a control system when conditions such as catalyst activity and heat transfer coefficients vary during operation.[6]

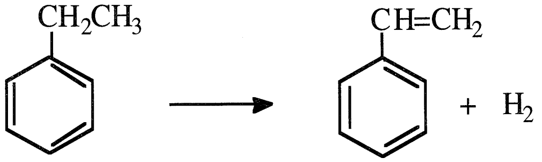
Ethylbenzene is mainly used to produce styrene. Over 90% of the 12.7 billion pounds of EB produced in the U.S. during 1998 was dehydrogenated to styrene.

Styrene



Styrene (vinylbenzene) is a liquid (b.p. 145.2°C) that polymerizes easily when initiated by a free radical or when exposed to light. The 1998 U.S. production of styrene was approximately 11 billion pounds.

1- Dehydrogenation of ethylbenzene to styrene occurs over a wide variety of metal oxide catalysts. Oxides of Fe, Cr, Si, Co, Zn, or their mixtures can be used for the dehydrogenation reaction. Typical reaction conditions for the vapor-phase process are 600–700°C, at or below atmospheric pressure. Approximately 90% styrene yield is obtained at 30–40% conversion:

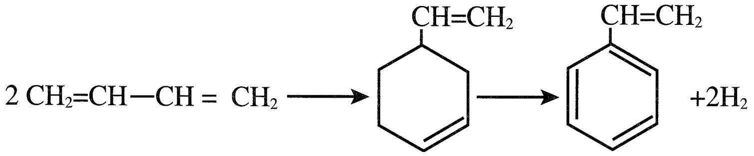


In the Monsanto/Lummus Crest process (Figure 10-3), fresh ethylbenzene with recycled unconverted ethylbenzene are mixed with superheated steam. The steam acts as a heating medium and as a diluent. The endothermic reaction is carried out in multiple radial bed reactors filled with proprietary catalysts. Radial beds minimize pressure drops across the reactor. A simulation and optimization of styrene plant based on the Lummus Monsanto process has been done by Sundaram et al.[7] Yields could be predicted, and with the help of an optimizer, the best operating conditions can be found. Figure 10-4 shows the effect of steam-to-EB ratio, temperature, and pressure on the equilibrium conversion of ethylbenzene.[7]

2- [illegible]

Alternative routes for producing styrene have been sought. One approach is to dimerize butadiene to 4-vinyl-1-cyclohexene, followed by catalytic dehydrogenation to styrene:[8]

3-



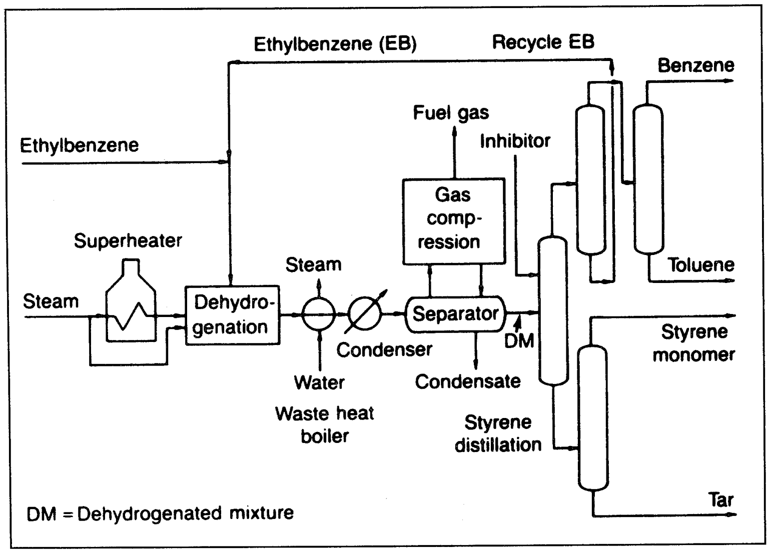
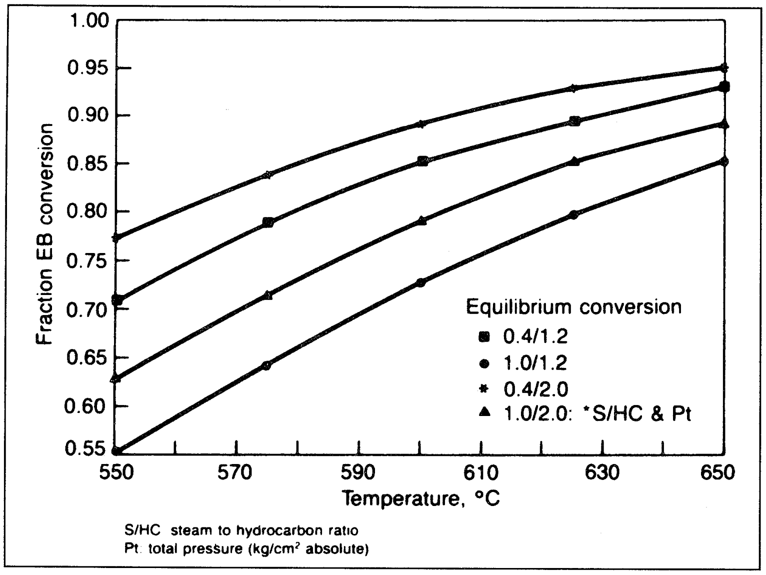


Figure 10-3. Schematic diagram of the Monsanto/Lummus Crest styrene plant.[7]

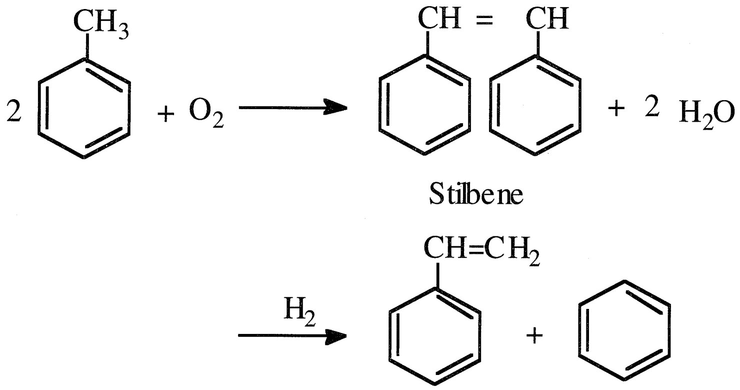


S/HC steam to hydrocarbon ratio
Pt total pressure (kg/cm^2 absolute)

Figure 10-4. Effect of steam/EB, temperature, and pressure on the conversion of ethylbenzene.[7]

The process which was developed by DOW involves cyclodimerization of butadiene over a proprietary copper-loaded zeolite catalyst at moderate temperature and pressure (100°C and 250 psig). To increase the yield, the cyclodimerization step takes place in a liquid phase process over the catalyst. Selectivity for vinylcyclohexene (VCH) was over 99%. In the second step VCH is oxidized with oxygen over a proprietary oxide catalyst in presence of steam. Conversion over 90% and selectivity to styrene of 92% could be achieved.[9]

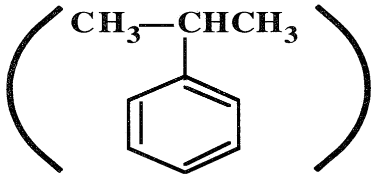
4- Another approach is the oxidative coupling of toluene to stilbene followed by disproportionation to styrene and benzene:



600°C

High temperatures are needed for this reaction, and the yields are low.

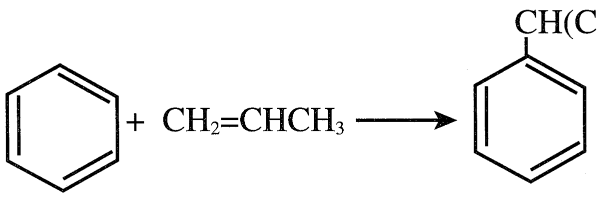
Cumene



Cumene (isopropylbenzene), a liquid, is soluble in many organic solvents but not in water. It is present in low concentrations in light refinery streams (such as reformates) and coal liquids. It may be obtained by distilling (cumene's B.P. is 152.7°C) these fractions.

The main process for producing cumene is a synthetic route where benzene is alkylated with propylene to isopropylbenzene.

Either a liquid or a gas-phase process is used for the alkylation reaction. In the liquid-phase process, low temperatures and pressures (approximately 50°C and 5 atmospheres) are used with sulfuric acid as a catalyst.



$\Delta H^{o}_{298} = -113$ KJ/mol

Small amounts of ethylene can be tolerated since ethylene is quite unreactive under these conditions. Butylenes are relatively unimportant because butylbenzene can be removed as bottoms from the cumene column.

In the vapor-phase process, the reaction temperature and pressure are approximately 250°C and 40 atmospheres. Phosphoric acid on Kieselguhr is a commonly used catalyst. To limit polyalkylation, a mixture of propene-propane feed is used. Propylene can be as low as 40% of the feed mixture. A high benzene/propylene ratio is also used to decrease polyalkylation. A selectivity of about 97% based on benzene can be obtained.

In the UOP process (Figure 10-5), fresh propylene feed is combined with fresh and recycled benzene, then passed through heat exchangers and a steam preheater before being charged to the reactor.[10] The effluent is separated, and excess benzene recycled. Cumene is finally clay treated and fractionated. The bottom product is mainly diisopropyl benzene, which is reacted with benzene in a transalkylation section:

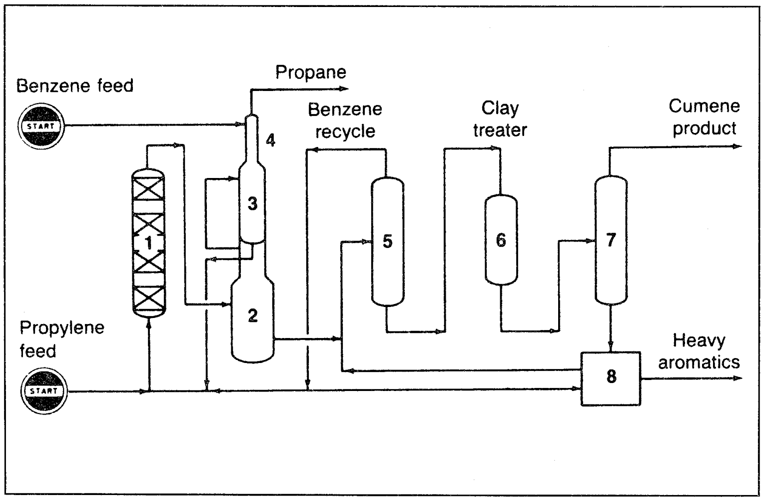
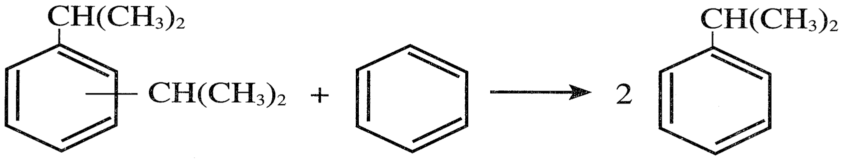
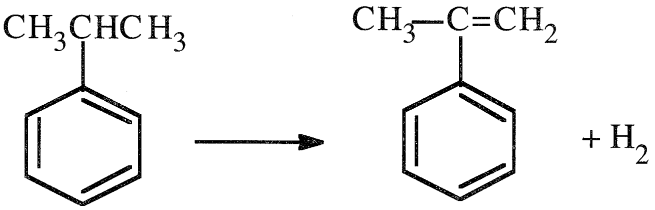


Figure 10-5. A flow diagram of the UOP cumene process:[10] (1) reactor, (2,3) two-stage flash system, (4) depropanizer, (5) benzene column, (6) clay treatment, (7) fractionator, (8) transalkylation section.



To reduce pollution, Dow developed a new catalyst system from the mordenite-zeolite group to replace phosophoric acid or aluminum chloride catalysts. The new catalysts eliminates the disposal of acid wastes and handling corrosive materials.[11]

The 1998 U.S. cumene production was approximately 6.7 billion pounds and was mainly used to produce phenol and acetone. A small amount of cumene is used to make α-methylstyrene by dehydrogenation.

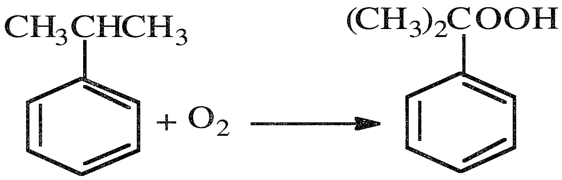


α-Methylstyrene

α-Methylstyrene is used as a monomer for polymer manufacture and as a solvent.

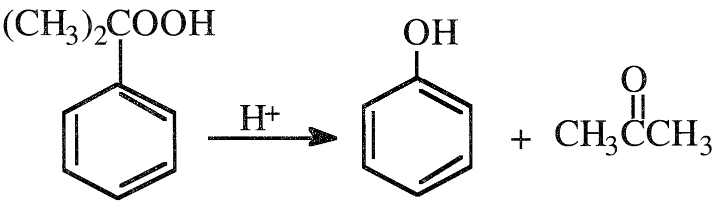
Phenol and Acetone from Cumene

Phenol, C_6H_5OH (hydroxybenzene), is produced from cumene by a two-step process. In the first step, cumene is oxidized with air to cumene hydroperoxide. The reaction conditions are approximately 100–130°C and 2–3 atmospheres in the presence of a metal salt catalyst:



$\Delta H = -116$ KJ/mol

In the second step, the hydroperoxide is decomposed in the presence of an acid to phenol and acetone. The reaction conditions are approximately 80°C and slightly below atmospheric:



In this process (Figure 10-6), cumene is oxidized in the liquid phase.[12] The oxidation product is concentrated to 80% cumene hydroperoxide by

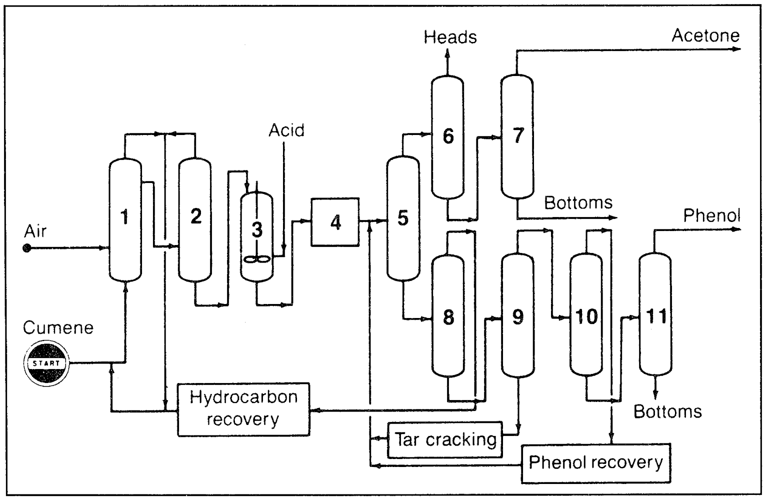


Figure 10-6. The Mitsui Petrochemical Industries process for producing phenol and acetone from cumene:[12] (1) autooxidation reactor, (2) vacuum tower, (3) cleavage reactor, (4) neutralizer, (5–11) purification train.

vacuum distillation. To avoid decomposition of the hydroperoxide, it is transferred immediately to the cleavage reactor in the presence of a small amount of H_2SO_4. The cleavage product is neutralized with alkali before it is finally purified.

After an initial distillation to split the coproducts phenol and acetone, each is purified in separate distillation and treating trains. An acetone finishing column distills product acetone from an acetone/water/oil mixture. The oil, which is mostly unreacted cumene, is sent to cumene recovery. Acidic impurities, such as acetic acid and phenol, are neutralized by caustic injection. Figure 10-7 is a simplified flow diagram of an acetone finishing column, and Table 10-1 shows the feed composition to the acetone finishing column.[13]

Cumene processes are currently the major source for phenol and coproduct acetone. Chapter 8 notes other routes for producing acetone.

Previously, phenol was produced from benzene by sulfonation followed by caustic fusion to sodium phenate. Phenol is released from the sodium salt of phenol by the action of carbon dioxide or sulfur dioxide.

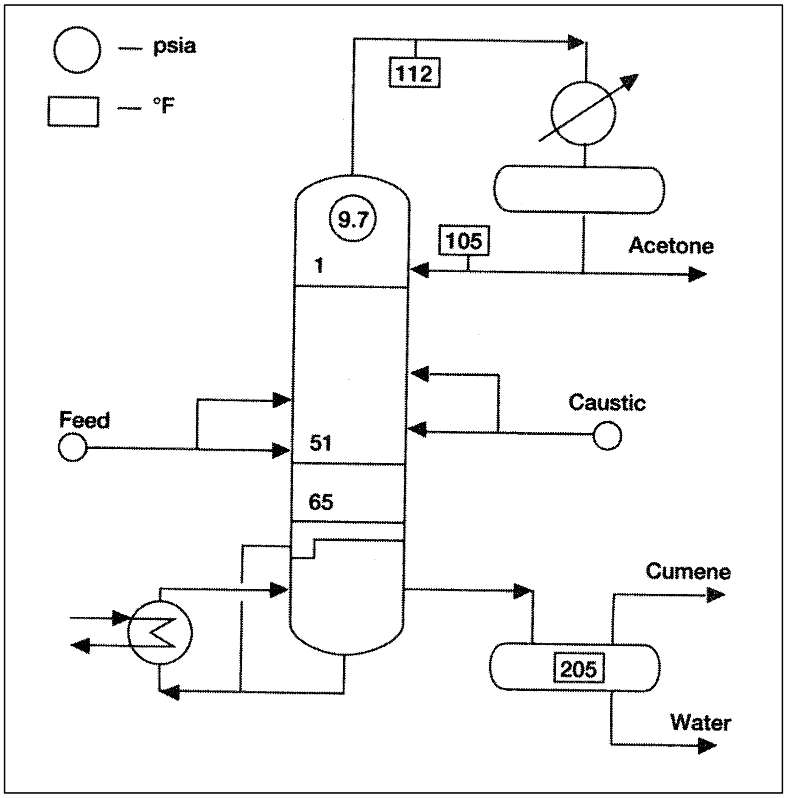


Figure 10-7. A simplified process flow chart of an acetone finishing column.[13]

Table 10-1
Feed composition of acetone finishing column[13]

Component	wt%
Acetone	48%
Water	22%
Cumene	24%
Alpha-methylstyrene and other heavy hydrocarbons	4%
Neutralized organics (sodium acetate, sodium phenate, etc.)	1%
Free caustic	1%

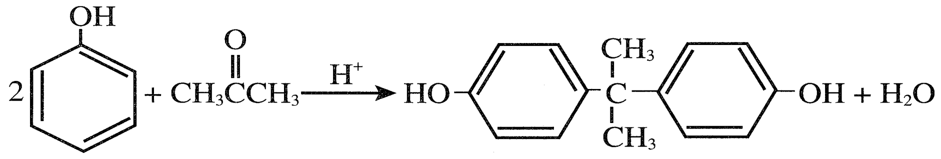
Direct hydroxylation of benzene to phenol could be achieved using zeolite catalysts containing rhodium, platinum, palladium, or irridium. The oxidizing agent is nitrous oxide, which is unavoidable a byproduct from the oxidation of KA oil (see KA oil, this chapter) to adipic acid using nitric acid as the oxidant.[14]

Phenol is also produced from chlorobenzene and from toluene via a benzoic acid intermediate (see "Reactions and Chemicals from Toluene").

Properties and Uses of Phenol

Phenol, a white crystalline mass with a distinctive odor, becomes reddish when subjected to light. It is highly soluble in water, and the solution is weakly acidic.

Phenol was the 33rd highest-volume chemical. The 1994 U.S. production of phenol was approximately 4 billion pounds. The current world capacity is approximately 15 billion pounds. Many chemicals and polymers derive from phenol. Approximately 50% of production goes to phenolic resins. Phenol and acetone produce bis-phenol A, an important monomer for epoxy resins and polycarbonates. It is produced by condensing acetone and phenol in the presence of HCl, or by using a cation exchange resin. Figure 10-8 shows the Chiyoda Corp. bisphenol A process.[15]



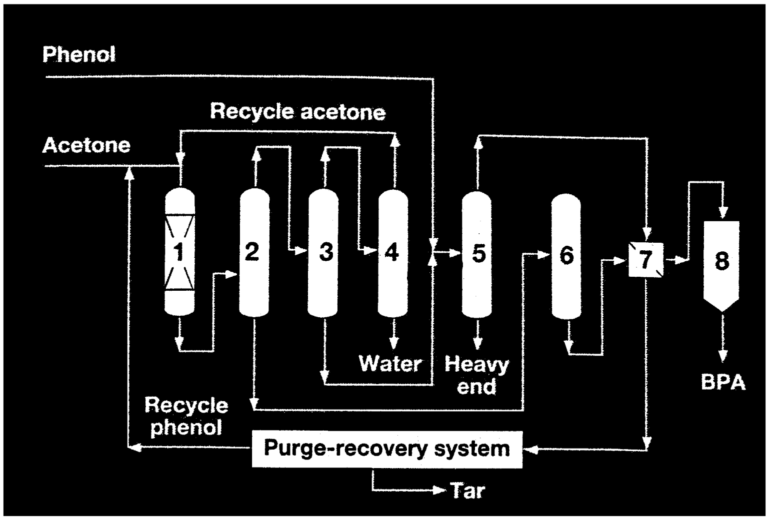
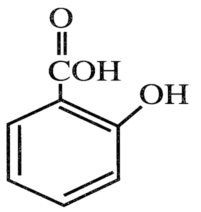
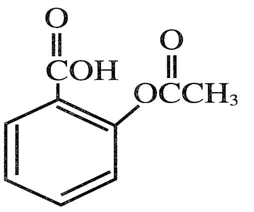


Figure 10-8. The CT-BISA (Chiyoda Corp.) process for producing bis-phenol A from acetone and phenol.[15] (1) reactor, (2–4) distillation columns, (5) phenol distillation column, (6) crystallizer, (7) solid/liquid separator, (8) prilling tower.

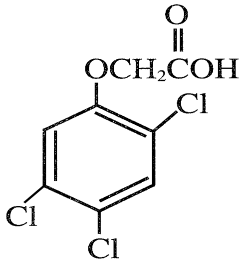
Important chemicals derived from phenol are salicylic acid; acetylsalicyclic acid (aspirin); 2,4-dichlorophenoxy acetic acid (2,4-D), and 2,4,5-triphenoxy acetic acid (2,4,5-T), which are selective herbicides; and pentachlorophenol, a wood preservative:



Salicyclic acid



Aspirin

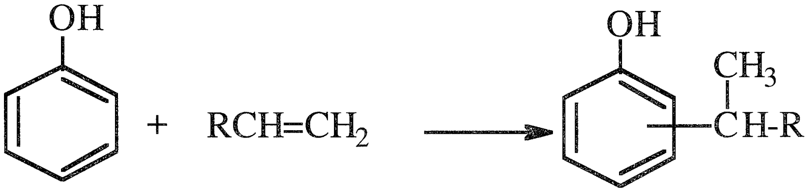


2,4,5-T

Other halophenols are miticides, bactericides, and leather preservatives. Halophenols account for about 5% of phenol uses.

About 12% of phenol demand is used to produce caprolactam, a monomer for nylon 6. The main source for caprolactam, however, is toluene.

Phenol can be alkylated to alkylphenols. These compounds are widely used as nonionic surfactants, antioxidants, and monomers in resin polymer applications:



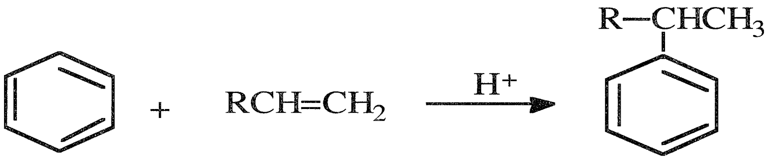
An alkylphenol

Phenol is also a precursor for aniline. The major process for aniline ($C_6H_5NH_2$) is the hydrogenation of nitrobenzene (see "Nitration of Benzene").

Linear Alkylbenzene

Linear alkylbenzene (LAB) is an alkylation product of benzene used to produce biodegradable anionic detergents. The alkylating agents are either linear C_{12}–C_{14} mono-olefins or monochloroalkanes. The linear olefins (alpha olefins) are produced by polymerizing ethylene using Ziegler catalysts (Chapter 7) or by dehydrogenating n-paraffins extracted from kerosines. Monochloroalkanes, on the other hand, are manufactured by chlorinating the corresponding n-paraffins. Dehydrogenation of n-paraffins to monoolefins using a newly developed dehydrogenation catalyst by UOP has been reviewed by Vora et al.[16] The new catalyst is highly active and allows a higher per-pass conversion to monoolefins. Because the dehydrogenation product contains a higher concentration of olefins for a given alkylate production rate, the total hydrocarbon feed to the HF alkylation unit is substantially reduced.[16]

Alkylation of benzene with linear monoolefins is industrially preferred. The Detal process (Figure 10-9) combines the dehydrogenation of n-paraffins and the alkylation of benzene.[17] Monoolefins from the dehydrogenation section are introduced to a fixed-bed alkylation reactor over a heterogeneous solid catalyst. Older processes use HF catalysts in a liquid phase process at a temperature range of 40–70°C. The general alkylation reaction of benzene using alpha olefins could be represented as:



Linear alkylbenzene (LAB)

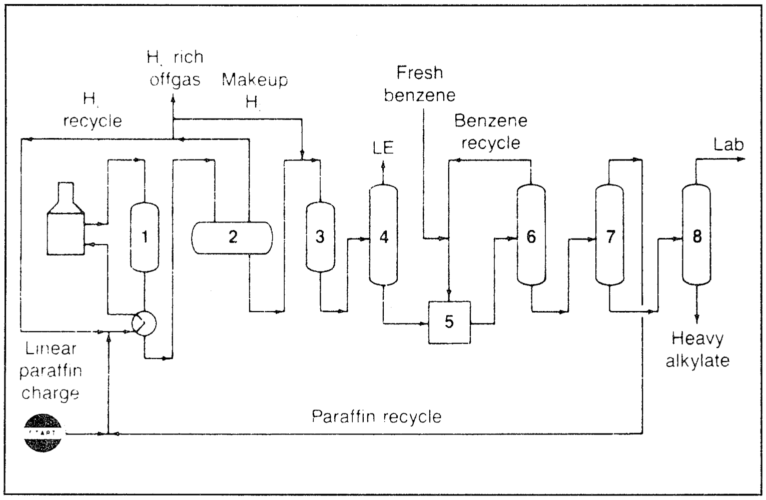
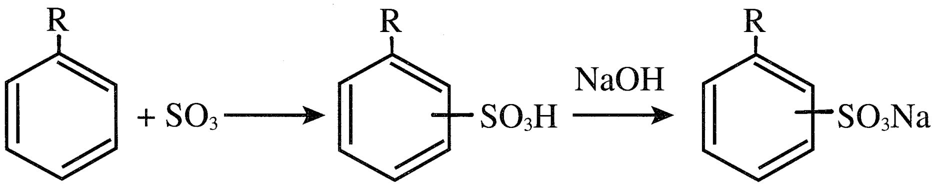


Figure 10-9. The UOP (Detal) process for producing linear alkylbenzene:[17] (1) pacol dehydrogenation reactor, (2) gas-liquid separation, (3) reactor for converting diolefins to monoolefins, (4) stripper, (5) alkylation reactor, (6,7,8) fractionators.

Typical properties of detergent alkylate are shown in Table 10-2.[16] Detergent manufacturers buy linear alkylbenzene, sulfonate it with SO_3, and then neutralize it with NaOH to produce linear alkylbenzene sulfonate (LABS), the active ingredient in detergents:

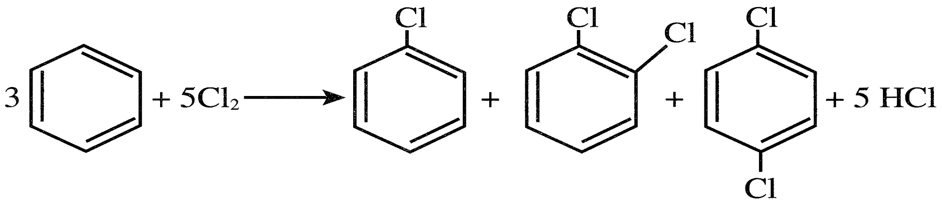


CHLORINATION OF BENZENE

Chlorination of benzene is an electrophilic substitution reaction in which Cl^+ serves as the electrophile. The reaction occurs in the presence of a Lewis acid catalyst such as $FeCl_3$. The products are a mixture of mono- and dichlorobenzenes. The *ortho*- and the *para*-dichlorobenzenes are more common than meta-dichlorobenzene. The ratio of the monochloro to dichloro products essentially depends on the benzene/chlorine ratio and the residence time. The ratio of the dichloro-isomers (*o*- to *p*- to *m*-dichlorobenzenes) mainly depends on the reaction temperature and residence time:

Table 10-2
Typical properties of detergent alkylate[16]

	Linear detergent alkylate
Bromine number	0.02
Saybolt color	+30
Alkylbenzene content, wt%	97.4
Doctor test	NEGATIVE
Unsulfonatable content, wt%	1.0
Water, wt%	0.1
Specific gravity at 60°F	0.8612
Refractive index, n^{20}_{D}	1.4837
Flash point (ASTM D-93), °F	280
Average molecular weight	240
Distillation (ASTM D-86), °F	
IBP	538
10 vol%	547
30 vol%	550
50 vol%	554
70 vol%	559
90 vol%	569
95 vol%	576
EP	589
Saybolt color of a 5% sodium alkylbenzene sulfonate solution	+26
Normal alkylbenzene, wt%	93
2-Phenyl isomer, wt%	20.0
Paraffin, wt%	0.1
Biodegradability (ASTM D-2667), %	>95.0

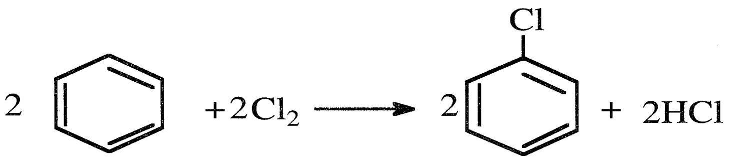


Typical liquid-phase reaction conditions for the chlorination of benzene using $FeCl_3$ catalyst are 80–100°C and atmospheric pressure. When a high benzene/Cl_2 ratio is used, the product mixture is approximately 80% monochlorobenzene, 15% *p*-dichlorobenzene and 5% *o*-dichlorobenzene.

Continuous chlorination processes permit the removal of monochlorobenzene as it is formed, resulting in lower yields of higher chlorinated benzene.

Monochlorobenzene is also produced in a vapor-phase process at approximately 300°C. The by-product HCl goes into a regenerative oxychlorination reactor. The catalyst is a promoted copper oxide on a silica carrier:

$$4\ HCl + O_2 \longrightarrow 2\ Cl_2 + 2\ H_2O$$



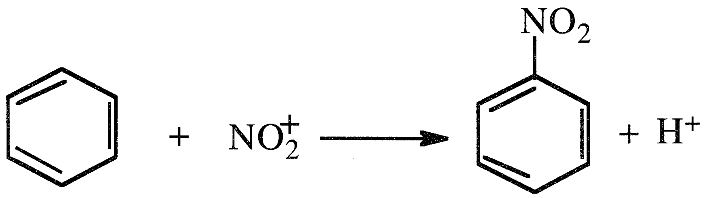
Higher conversions have been reported when temperatures of 234–315°C and pressures of 40–80 psi are used.[18]

Monochlorobenzene is the starting material for many compounds, including phenol and aniline. Others, such as DDT, chloronitrobenzenes, polychlorobenzenes, and biphenyl, do not have as high a demand for monochlorobenzene as aniline and phenol.

NITRATION OF BENZENE (Nitrobenzene [$C_6H_5NO_2$])

Similar to the alkylation and the chlorination of benzene, the nitration reaction is an electrophilic substitution of a benzene hydrogen (a proton) with a nitronium ion (NO_2^+). The liquid-phase reaction occurs in presence of both concentrated nitric and sulfuric acids at approximately 50°C. Concentrated sulfuric acid has two functions: it reacts with nitric acid to form the nitronium ion, and it absorbs the water formed during the reaction, which shifts the equilibrium to the formation of nitrobenzene:

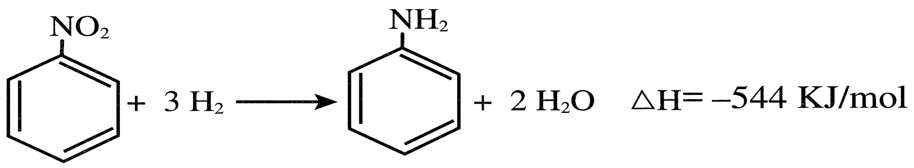
$$HNO_3 + 2H_2SO_4 \longrightarrow 2\ HSO_4^- + H_3O^+ + NO_2^+$$



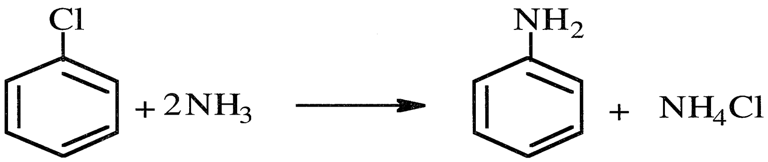
Most of the nitrobenzene (≈97%) produced is used to make aniline. Other uses include synthesis of quinoline, benzidine, and as a solvent for cellulose ethers.

Aniline ($C_6H_5NH_2$)

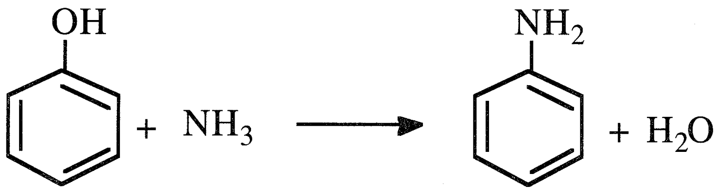
Aniline (aminobenzene) is an oily liquid that turns brown when exposed to air and light. The compound is an important dye precursor. The main process for producing aniline is the hydrogenation of nitrobenzene:



The hydrogenation reaction occurs at approximately 270°C and slightly above atmospheric over a Cu/Silica catalyst. About a 95% yield is obtained. An alternative way to produce aniline is through ammonolysis of either chlorobenzene or phenol. The reaction of chlorobenzene with aqueous ammonia occurs over a copper salt catalyst at approximately 210°C and 65 atmospheres. The yield of aniline from this route is also about 96%:



Ammonolysis of phenol occurs in the vapor phase. In the Scientific Design Co. process (Figure 10-10), a mixed feed of ammonia and phenol is heated and passed over a heterogeneous catalyst in a fixed-bed system.[19] The reactor effluent is cooled, the condensed material distilled, and the unreacted ammonia recycled. Aniline produced this way should be very pure:



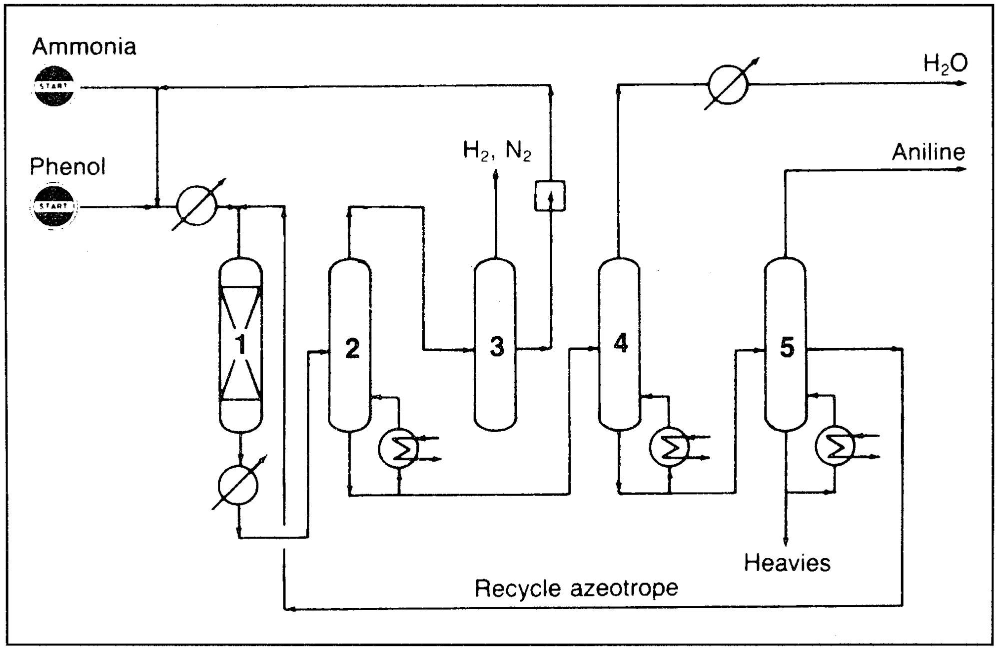
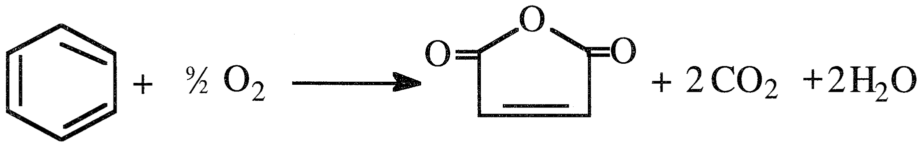


Figure 10-10. The Scientific Co. process for producing aniline from phenol:[19] (1) fixed-bed reactor, (2) liquid-gas separator, (3) ammonia compression and recycling, (4) drier, (5) fractionator.

Lecture 7

OXIDATION OF BENZENE

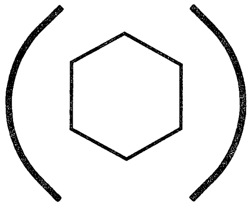
Benzene oxidation is the oldest method to produce maleic anhydride. The reaction occurs at approximately 380°C and atmospheric pressure. A mixture of V_2O_5/MO_3 is the usual catalyst. Benzene conversion reaches 90%, but selectivity to maleic anhydride is only 50–60%; the other 40–50% is completely oxidized to CO_2:[20]



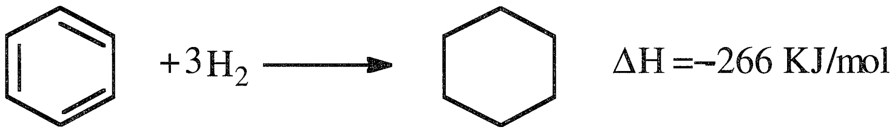
Currently, the major route to maleic anhydride, especially for the newly-erected processes, is the oxidation of butane (Chapter 6). Maleic anhydride also comes from oxidation of n-butenes. Properties and chemicals derived from maleic anhydride are noted in Chapter 9.

HYDROGENATION OF BENZENE

Cyclohexane



The hydrogenation of benzene produces cyclohexane. Many catalyst systems, such as Ni/alumina and Ni/Pd, are used for the reaction. General reaction conditions are 160–220°C and 25–30 atmospheres. Higher temperatures and pressures may also be used with sulfided catalysts:



Older methods use a liquid phase process (Figure 10-11).[10] New gas-phase processes operate at higher temperatures with noble metal catalysts. Using high temperatures accelerates the reaction (faster rate).[21] The hydrogenation of benzene to cyclohexane is characterized by a highly exothermic reaction and a significant decrease in the product volume

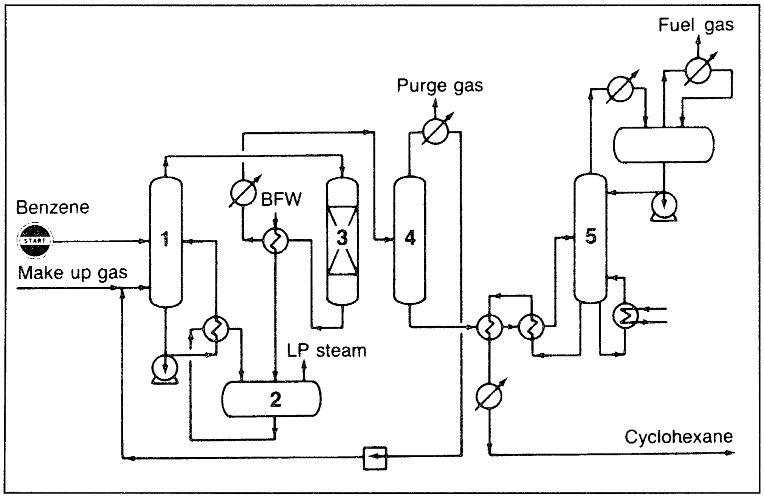


Figure 10-11. The Institut Francais du Petrole process for the hydrogenation of benzene to cyclohexane:[10] (1) liquid-phase reactor, (2) heat exchanger, (3) catalytic pot (acts as a finishing reactor when conversion of the main reactor drops below the required level), (4) high-pressure separator, (5) stabilizer.

(from 4 to 1). Equilibrium conditions are therefore strongly affected by temperature and pressure. Figure 10-12 shows the effect of H_2/benzene mole ratio on the benzene content in the products.[21] It is clear that benzene content in the product decreases with an increase of the reactor inlet pressure.

Another nonsynthetic source for cyclohexane is natural gasoline and petroleum naphtha. However, only a small amount is obtained from this source. The 1994 U.S. production of cyclohexane was approximately 2.1 billion pounds (the 45th highest chemical volume).

Properties and Uses of Cyclohexane

Cyclohexane is a colorless liquid, insoluble in water but soluble in hydrocarbon solvents, alcohol, and acetone. As a cyclic paraffin, it can be easily dehydrogenated to benzene. The dehydrogenation of cyclohexane

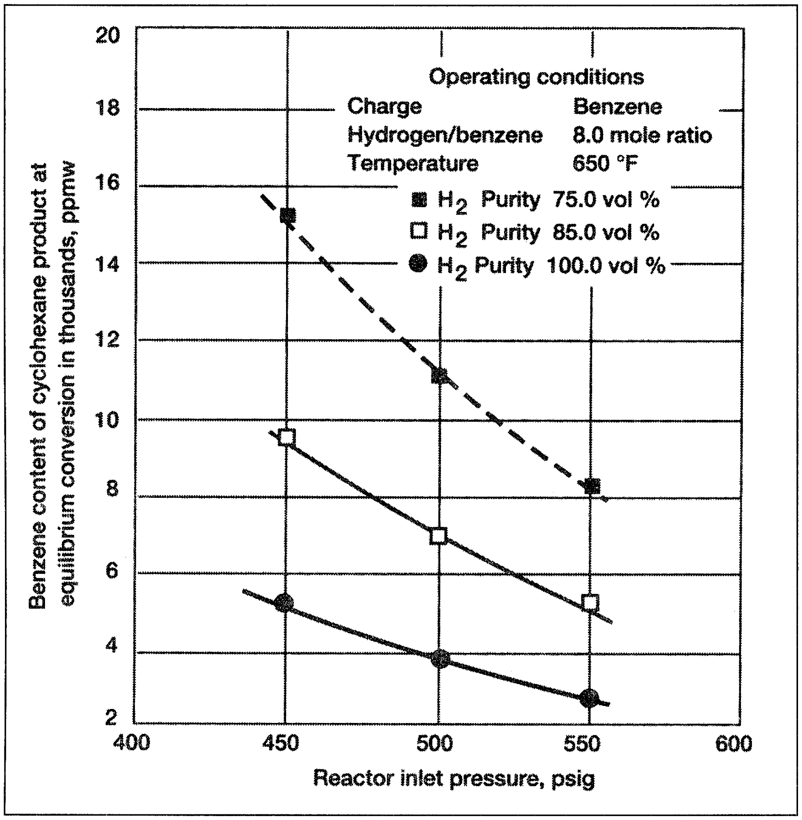


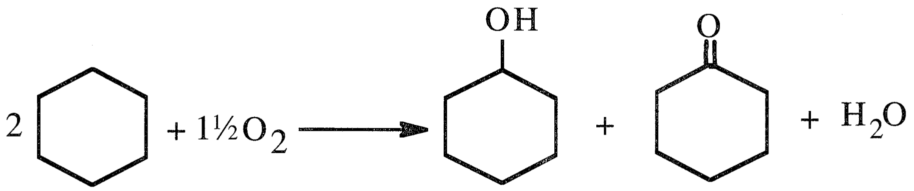
Figure 10-12. Effect of hydrogen purity and pressure on benzene conversion to cyclohexane.[21]

and its derivatives (present in naphthas) to aromatic hydrocarbons is an important reaction in the catalytic reforming process.

Essentia]ly, all cyclohexane is oxidized either to a cyclohexanone-cyclohexanol mixture used for making caprolactam or to adipic acid. These are monomers for making nylon 6 and nylon 6/6.

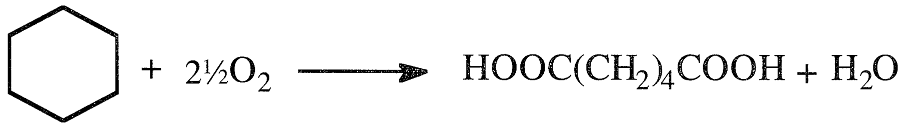
Oxidation of Cyclohexane (Cyclohexanone-Cyclohexanol and Adipic Acid)

Cyclohexane is oxidized in a liquid-phase process to a mixture of cyclohexanone and cyclohexanol (KA oil). The reaction conditions are 95–120°C at approximately 10 atmospheres in the presence of a cobalt acetate and orthoboric acid catalyst system. About 95% yield can be obtained:



KA oil is used to produce caprolactam, the monomer for nylon 6. Caprolactam is also produced from toluene through the intermediate formation of cyclohexane carboxylic acid.

Cyclohexane is also a precursor for adipic acid. Oxidizing cyclohexane in the liquid-phase at lower temperatures and for longer residence times (than for KA oil) with a cobalt acetate catalyst produces adipic acid:



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Adipic acid may also be produced from butadiene via a carbonylation route (Chapter 9).

Adipic acid and its esters are used to make nylon 6/6. It may also be hydrogenated to 1,6-hexanediol, which is further reacted with ammonia to hexamethylenediamine.

$$HOOC(CH_2)_4COOH + 4H_2 \rightarrow HO(CH_2)_6OH + 2H_2O$$

$$HO(CH_2)_6OH + 2NH_3 \rightarrow H_2N(CH_2)_6NH_2 + 2H_2O$$

Hexamethylenediamine is the second monomer for nylon 6/6.

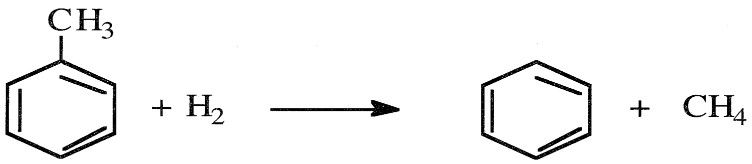
REACTIONS AND CHEMICALS OF TOLUENE

Toluene (methylbenzene) is similar to benzene as a mononuclear aromatic, but it is more active due to presence of the electron-donating methyl group. However, toluene is much less useful than benzene because it produces more polysubstituted products. Most of the toluene extracted for chemical use is converted to benzene via dealkylation or disproportionation. The rest is used to produce a limited number of petrochemicals. The main reactions related to the chemical use of toluene (other than conversion to benzene) are the oxidation of the methyl substituent and the hydrogenation of the phenyl group. Electrophilic substitution is limited to the nitration of toluene for producing mononitrotoluene and dinitrotoluenes. These compounds are important synthetic intermediates.

The 1994 U.S. toluene production (of all grades) was approximately 6.8 billion pounds. Hydrodealkylating toluene to benzene was the largest end use in United States and West Europe, followed by solvent applications.

DEALKYLATION OF TOLUENE

Toluene is dealkylated to benzene over a hydrogenation-dehydrogenation catalyst such as nickel. The hydrodealkylation is essentially a hydrocracking reaction favored at higher temperatures and pressures. The reaction occurs at approximately 700°C and 40 atmospheres. A high benzene yield of about 96% or more can be achieved:

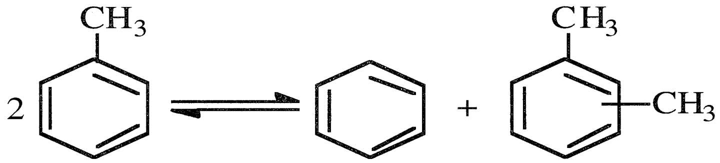


Hydrodealkylation of toluene and xylenes with hydrogen is noted in Chapter 3.

Dealkylation also can be effected by steam. The reaction occurs at 600–800°C over Y, La, Ce, Pr, Nd, Sm, or Th compounds, Ni-Cr_2O_3 catalysts, and Ni-Al_2O_3 catalysts at temperatures between 320–630°C.[22] Yields of about 90% are obtained. This process has the advantage of producing, rather than using, hydrogen.

DISPROPORTIONATION OF TOLUENE

The catalytic disproportionation of toluene (Figure 10-13)[23] in the presence of hydrogen produces benzene and a xylene mixture. Disproportionation is an equilibrium reaction with a 58% conversion per pass theoretically possible. The reverse reaction is the transalkylation of xylenes with benzene:



Typical conditions for the disproportionation reaction are 450–530°C and 20 atmospheres. A mixture of CoO-MoO_3 on aluminosilicates/alumina catalysts can be used. Conversions of approximately 40% are normally used to avoid more side reactions and faster catalyst deactivation.[24] The equilibrium constants for this reaction are not significantly changed by shifting from liquid to vapor phase or by large temperature changes.[25]

Currently, zeolites, especially those of ZSM-5 type, are preferred for their higher activities and selectivities. They are also more stable thermally. Modifying ZSM-5 zeolites with phosphorous, boron, or

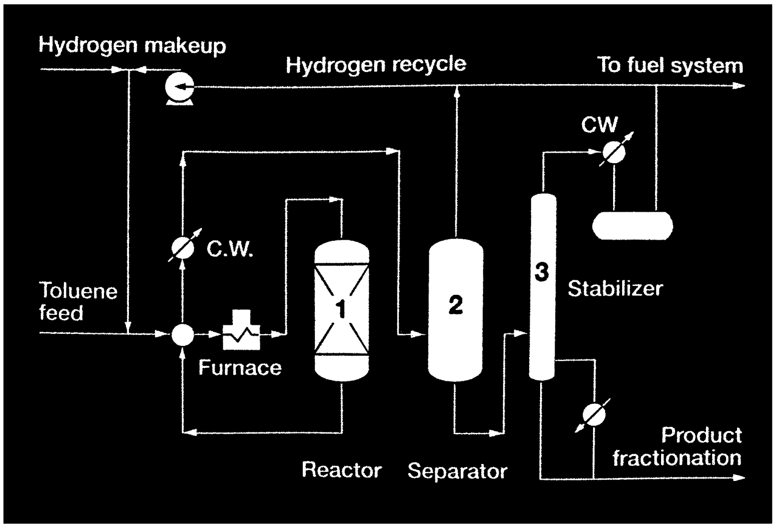
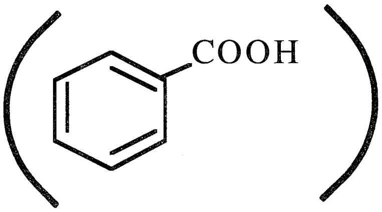


Figure 10-13. The Mobil Oil Corp., IFP process for the disproportionation of toluene to mixed xylenes.[23]

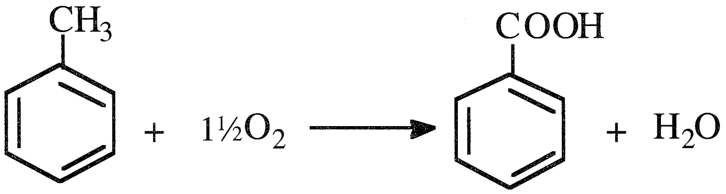
magnesium compounds produces xylene mixtures rich in the p-isomer (70–90%). It has been proposed that the oxides of these elements, present in zeolites, reduce the dimensions of the pore openings and channels and so favor formation and outward diffusion of p-xylene, the isomer with the smallest minimum dimension.[26,27]

OXIDATION OF TOLUENE

Benzoic Acid



Oxidizing toluene in the liquid phase over a cobalt acetate catalyst produces benzoic acid. The reaction occurs at about 165°C and 10 atmospheres. The yield is over 90%:



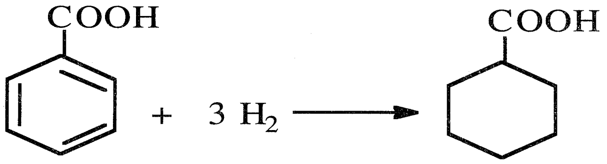
Benzoic acid (benzene carboxylic acid) is a white crystalline solid with a characteristic odor. It is slightly soluble in water and soluble in most common organic solvents.

Though much benzoic acid gets used as a mordant in calico printing, it also serves to season tobacco, preserve food, make dentifrices, and kill fungus. Furthermore it is a precursor for caprolactam, phenol, and terephthalic acid.

Caprolactam Production

Caprolactam, a white solid that melts at 69°C, can be obtained either in a fused or flaked form. It is soluble in water, ligroin, and chlorinated hydrocarbons. Caprolactam's main use is to produce nylon 6. Other minor uses are as a crosslinking agent for polyurethanes, in the plasticizer industry, and in the synthesis of lysine.

The first step in producing caprolactam from benzoic acid is its hydrogenation to cyclohexane carboxylic acid at approximately 170°C and 16 atmospheres over a palladium catalyst:[28]



The resulting acid is then converted to caprolactam through a reaction with nitrosyl-sulfuric acid:

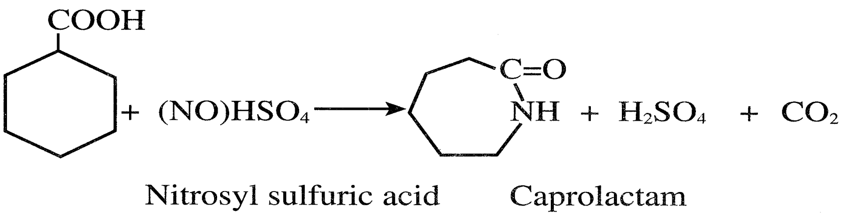


Figure 10-14 shows an integrated caprolactam production process.[28] Toluene, the feed, is first oxidized to benzoic acid. Benzoic acid is then hydrogenated to cyclohexane carboxylic acid, which reacts with nitrosyl-sulfuric acid yielding caprolactam. Nitrosyl sulfuric acid comes from reacting nitrogen oxides with oleum. Caprolactam comes as an acidic solution that is neutralized with ammonia and gives ammonium sulfate as

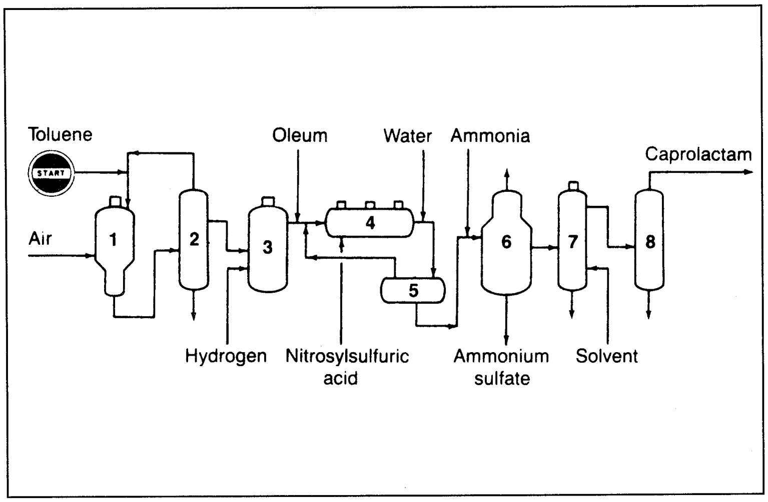
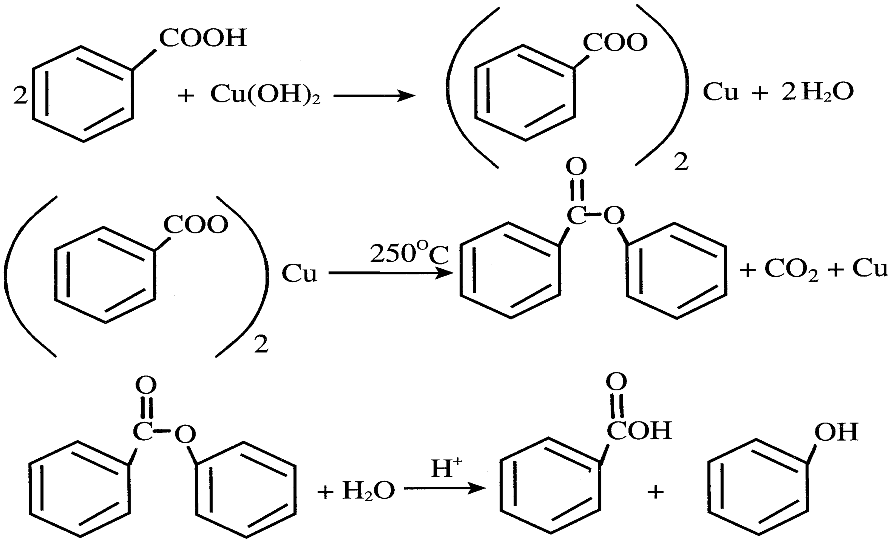


Figure 10-14. The SNIA BPD process for producing caprolactam:[28] (1) toluene oxidation reactor, (2) fractionator, (3) hydrogenation reactor (stirred autoclave), (4) multistage reactor (conversion to caprolactam), (5) water dilution, (6) crystallizer, (7) solvent extraction, (8) fractionator.

a by-product of commercial value. Recovered caprolactam is purified through solvent extraction and fractionation.

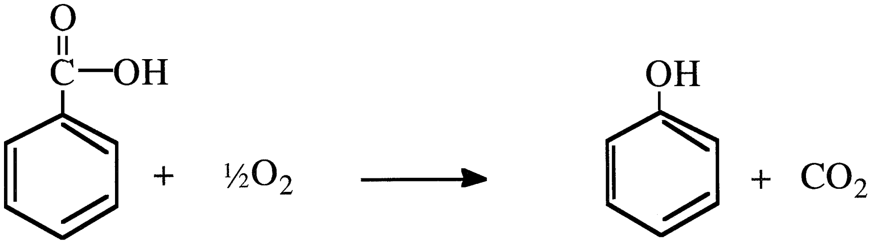
Phenol from Benzoic Acid

The action of a copper salt converts benzoic acid to phenol. The copper, reoxidized by air, functions as a real catalyst. The Lummus process operates in the vapor phase at approximately 250°C. Phenol yield of 90% is possible:



$$Cu + \tfrac{1}{2}O_2 + H_2O \longrightarrow Cu(OH)_2$$

The overall reaction is



In the Lummus process (Figure 10-15), the reaction occurs in the liquid phase at approximately 220–240°C over $Mg^{2+} + Cu^{2+}$ benzoate.[29] Magnesium benzoate is an initiator, with the Cu^{2+} reduced to Cu^{1+}. The copper (1) ions are reoxidized to copper (II) ions.

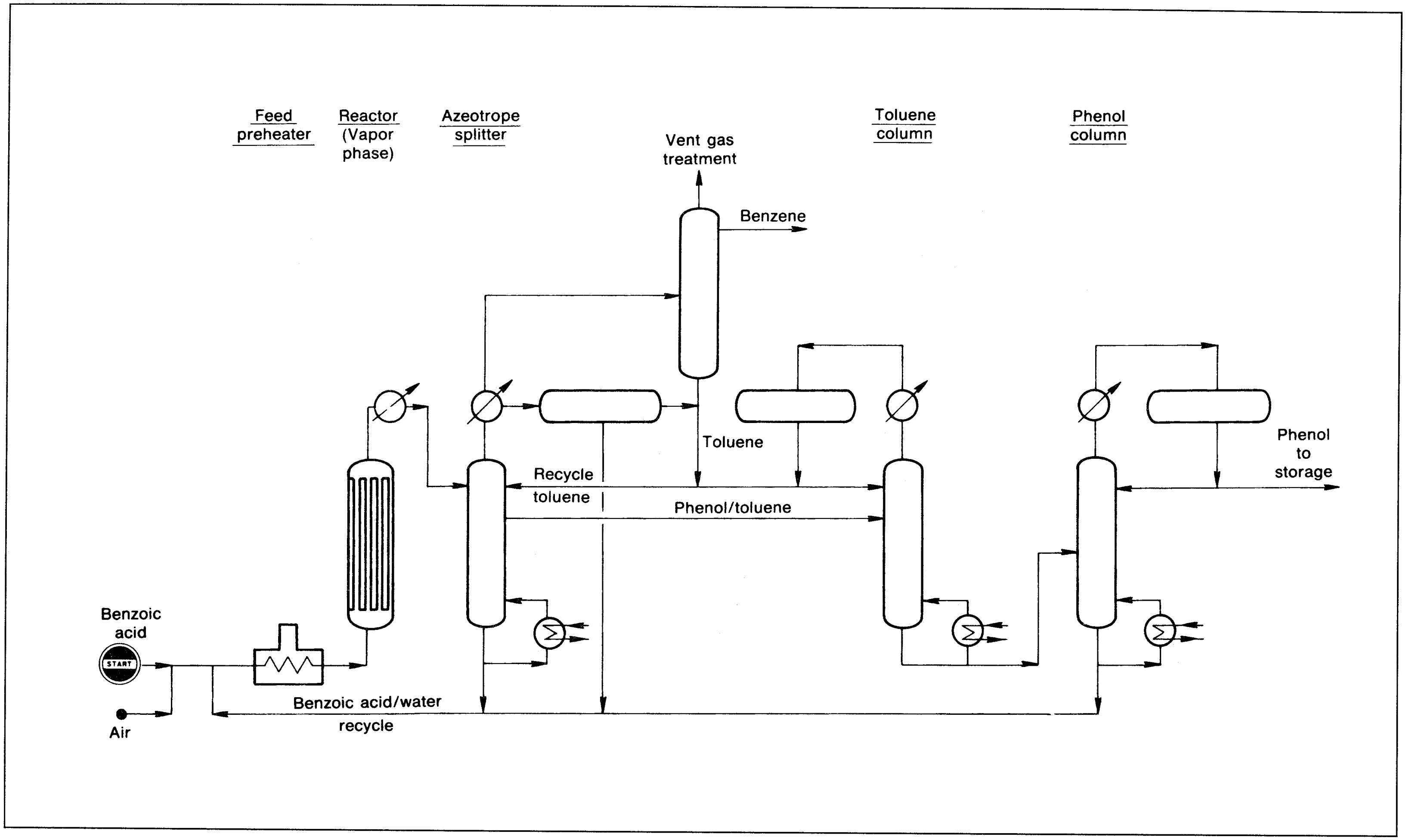


Figure 10-15. The Lummus benzoic-acid-to-phenol process.[29]

CHEMICALS FROM XYLENES

Xylenes (dimethylbenzenes) are an aromatic mixture composed of three isomers (*o*-, *m*-, and *p*-xylene). They are normally obtained from catalytic reforming and cracking units with other C_6, C_7, and C_8 aromatics. Separating the aromatic mixture from the reformate is done by extraction-distillation and isomerization processes (Chapter 2).

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para-Xylene is the most important of the three isomers for producing terephthalic acid to manufacture polyesters. *m*-Xylene is the least used of the three isomers, but the equilibrium mixture obtained from catalytic reformers has a higher ratio of the meta isomer. Table 10-3 shows the thermodynamic composition of C_8 aromatics at three temperatures.[32] *m*-Xylene is usually isomerized to the more valuable *p*-xylene.

As mentioned earlier, xylene chemistry is primarily related to the methyl substituents, which are amenable to oxidation.

Approximately 65% of the isolated xylenes are used to make chemicals. The rest are either used as solvents or blended with gasolines. The 1998 U.S. production of mixed xylenes for chemical use was approximately 9.5 million pounds. *p*-Xylene alone was about 7.7 million pounds that year.

TEREPHTHALIC ACID ($HOOCC_6H_4COOH$)

The catalyzed oxidation of *p*-xylene produces terephthalic acid (TPA). Cobalt acetate promoted with either NaBr or HBr is used as a catalyst in an acetic acid medium. Reaction conditions are approximately 200°C and 15 atmospheres. The yield is about 95%:

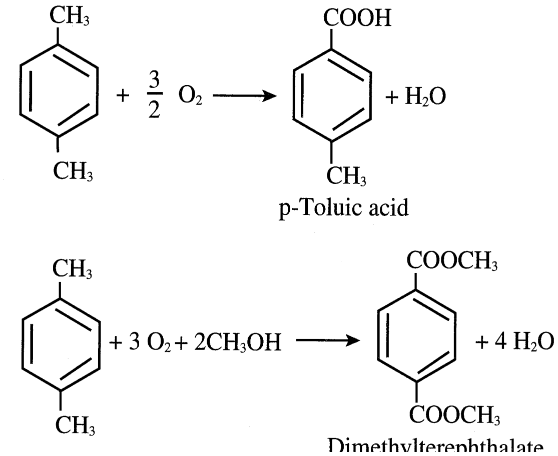

Table 10-3
Thermodynamic equilibrium composition of C_8 aromatics at three temperatures[32]

		Composition	
Aromatics wt%	200°C	300°C	500°C
p-Xylene	21.8	21.1	18.9
o-Xylene	20.6	21.6	23.0
m-Xylene	53.5	51.1	47.1
Ethylbenzene	4.1	6.2	11.0

Special precautions must be taken so that the reaction does not stop at the *p*-toluic acid stage. One approach is to esterify toluic acid as it is formed with methanol. This facilitates the oxidation of the second methyl group. The resulting dimethyl terephthalate (DMT) may be hydrolyzed to terephthalic acid.

Another approach is to use an easily oxidized substance such as acetaldehyde or methylethyl ketone, which, under the reaction conditions, forms a hydroperoxide. These will accelerate the oxidation of the second methyl group. The DMT process encompasses four major processing steps: oxidation, esterification, distillation, and crystallization. Figure 10-16 shows a typical *p*-xylene oxidation process to produce terephthalic acid or dimethyl terephthalate.[33] The main use of TPA and DMT is to produce polyesters for synthetic fiber and film.

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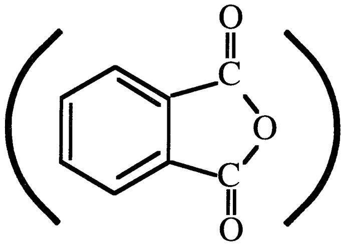
Phthalic Anhydride



Currently, phthalic anhydride is mainly produced through catalyzed oxidation of *o*-xylene. A variety of metal oxides are used as catalysts. A typical one is $V_2O_5 + TiO_2/Sb_2O_3$. Approximate conditions for the vapor-phase oxidation are 375–435°C and 0.7 atmosphere. The yield of phthalic anhydride is about 85%:

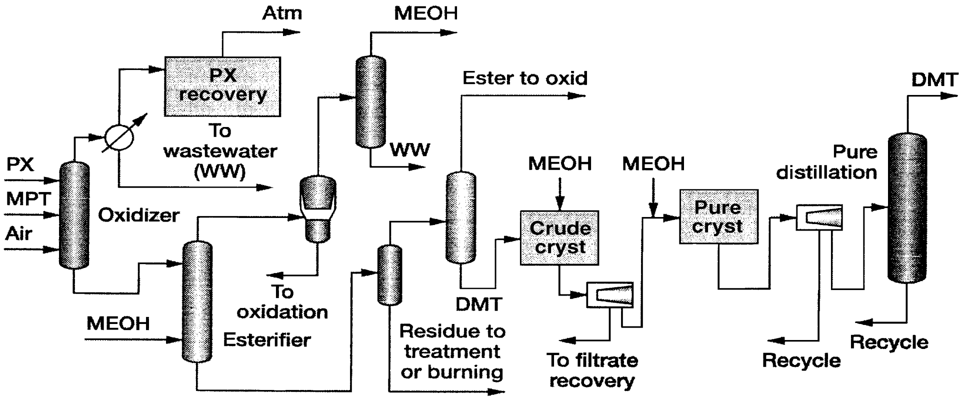
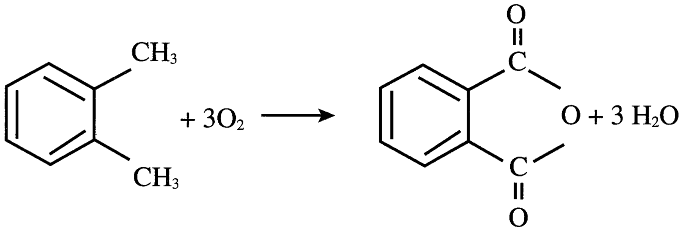


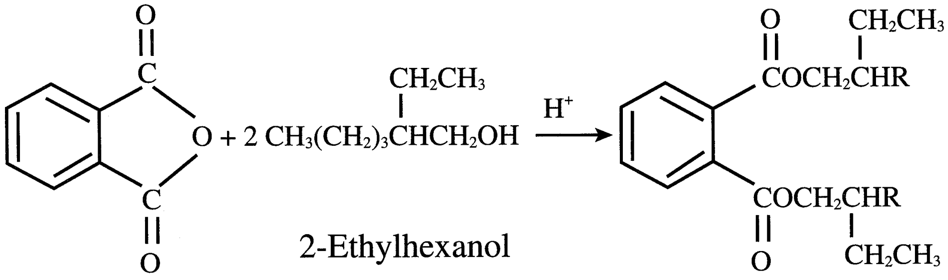
Figure 10-16. A typical *p*-xylene to dimethyl terephthalate process.[33]



Liquid-phase oxidation of *o*-xylene also works at approximately 150°C. Cobalt or manganese acetate in acetic acid medium serves as a catalyst.

The major by-products of this process are maleic anhydride, benzoic acid, and citraconic anhydride (methylmaleic anhydride). Maleic anhydride could be recovered economically.[34]

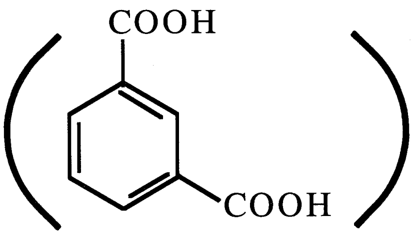
Phthalic anhydride's main use is for producing plasticizers by reactions with C_4–C_{10} alcohols. The most important polyvinyl chloride plasticizer is formed by the reaction of 2-ethylhexanol (produced via butyraldehyde, Chapter 8) and phthalic anhydride:



$R = CH_3(CH_2)_3$-

Phthalic anhydride is also used to make polyester and alkyd resins. It is a precursor for phthalonitrile by an ammoxidation route used to produce phthalamide and phathilimide. The reaction scheme for producing phthalonitrile, phthalamide, and phathilimide is shown in Figure 10-17.[34]

Isophthalic Acid



The oxidation of *m*-xylene produces isophthalic acid. The reaction occurs in the liquid-phase in presence of ammonium sulfite:

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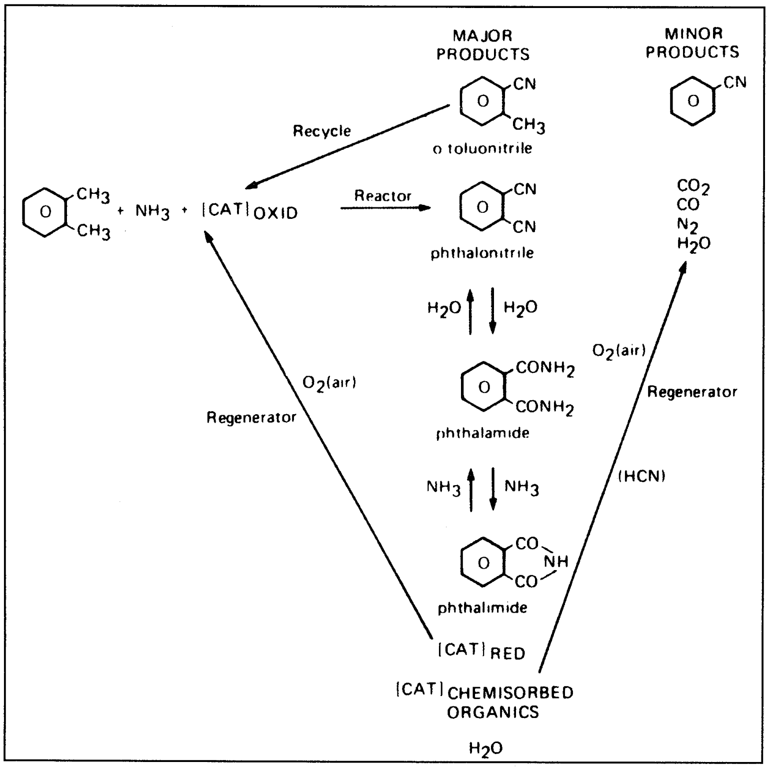
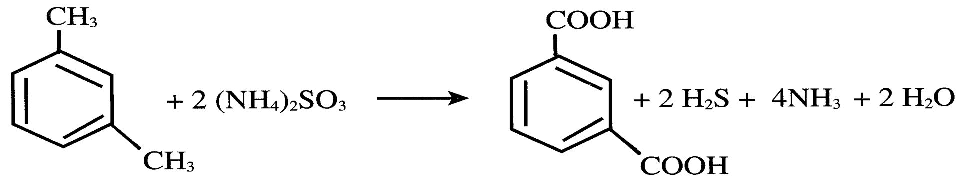


Figure 10-17. The reaction scheme for *o*-xylene to phthalonitrile.[34]



Isophthalic acid's main use is for producing polyesters that are characterized by a higher abrasion resistance than those using other phthalic acids. Polyesters from isophthalic acid are used for pressure molding applications.? why

Ammoxidation of isophthalic acid produces isophthalonitrile. The reaction resembles the one used for ammoxidation of phthalic anhydride:

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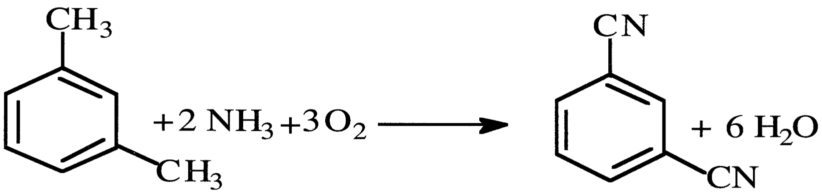


Isophthalonitrile

Isophthalonitrile serves as a precursor for agricultural chemicals. It is readily hydrogenated to the corresponding diamine, which can form polyamides or be converted to isocyanates for polyurethanes.

REFERENCES

Lecture 8

Chemicals Based on Methane

INTRODUCTION

As mentioned in Chapter 2, methane is a one-carbon paraffinic hydrocarbon that is not very reactive under normal conditions. Only a few chemicals can be produced directly from methane under relatively severe conditions. Chlorination of methane is only possible by thermal or photochemical initiation. Methane can be partially oxidized with a limited amount of oxygen or in presence of steam to a synthesis gas mixture. Many chemicals can be produced from methane via the more reactive synthesis gas mixture. Synthesis gas is the precursor for two major chemicals, ammonia and methanol. Both compounds are the hosts for many important petrochemical products. Figure 5-1 shows the important chemicals based on methane, synthesis gas, methanol, and ammonia.[1]

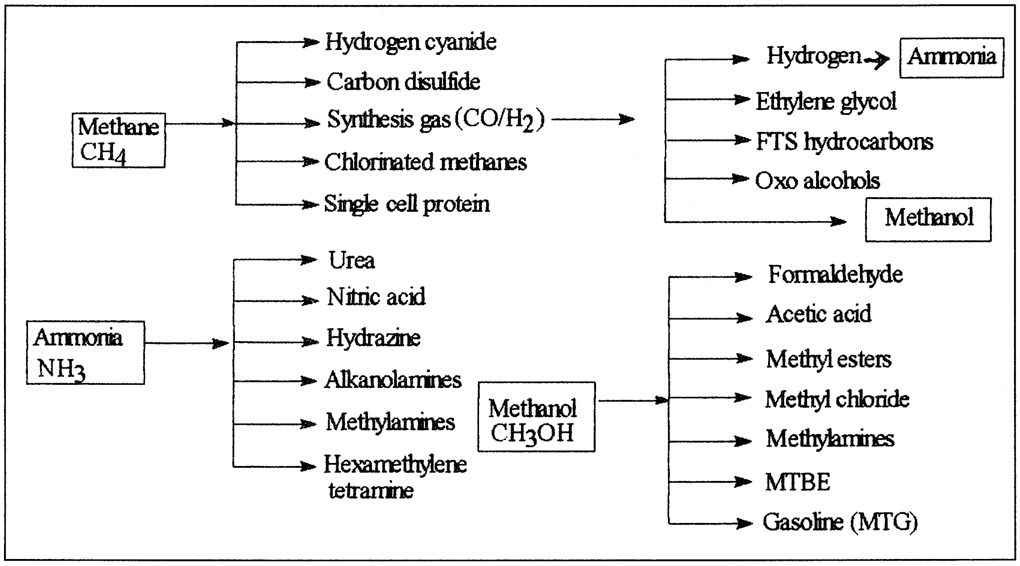


Figure 5-1. Important chemicals based on methane, synthesis gas, ammonia, and methanol.[1]

CHEMICALS BASED ON DIRECT REACTIONS OF METHANE

A few chemicals are based on the direct reaction of methane with other reagents. These are carbon disulfide, hydrogen cyanide chloromethanes, and synthesis gas mixture. Currently, a redox fuel cell based on methane is being developed.[2]

CARBON DISULFIDE (CS_2)

Methane reacts with sulfur (an active nonmetal element of group 6A) at high temperatures to produce carbon disulfide. The reaction is endothermic, and an activation energy of approximately 160 KJ is required.[3] Activated alumina or clay is used as the catalyst at approximately 675°C and 2 atmospheres. The process starts by vaporizing pure sulfur, mixing it with methane, and passing the mixture over the alumina catalyst. The reaction could be represented as:

$$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g) \qquad \Delta H^{\circ}_{298} = +150 \text{ KJ/mol}$$

Hydrogen sulfide, a coproduct, is used to recover sulfur by the Claus reaction. A CS_2 yield of 85–90% based on methane is anticipated. An alternative route for CS_2 is by the reaction of liquid sulfur with charcoal. However, this method is not used very much.

Uses of Carbon Disulfide

Carbon disulfide is primarily used to produce rayon and cellophane (regenerated cellulose). CS_2 is also used to produce carbon tetrachloride using iron powder as a catalyst at 30°C:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

Sulfur monochloride is an intermediate that is then reacted with carbon disulfide to produce more carbon tetrachloride and sulfur:

$$2S_2Cl_2 + CS_2 \rightarrow CCl_4 + 6S$$

The net reaction is:

$$CS_2 + 2Cl_2 \rightarrow CCl_4 + 2S$$

Chloromethane

Chloromethane namely methyl chloride (CH3Cl), methylene chloride (CH2Cl2), Chloroform (CHCl3) and Carbon Tetrachloride (CCl4) are produced by direct chlorination of Cl2 in a gas phase reaction without any catalyst.

Reactions

$$\mathrm{CH4} + \mathrm{Cl2} \rightarrow \mathrm{CH3Cl} + \mathrm{HCl}$$

$$\mathrm{CH3Cl} + \mathrm{Cl2} \rightarrow \mathrm{CH2Cl2} + \mathrm{HCl}$$

$$\mathrm{CH2Cl2} + \mathrm{Cl2} \rightarrow \mathrm{CHCl3} + \mathrm{HCl}$$

$$\mathrm{CHCl3} + Cl2 \rightarrow \mathrm{CCl4} + \mathrm{HCl}$$

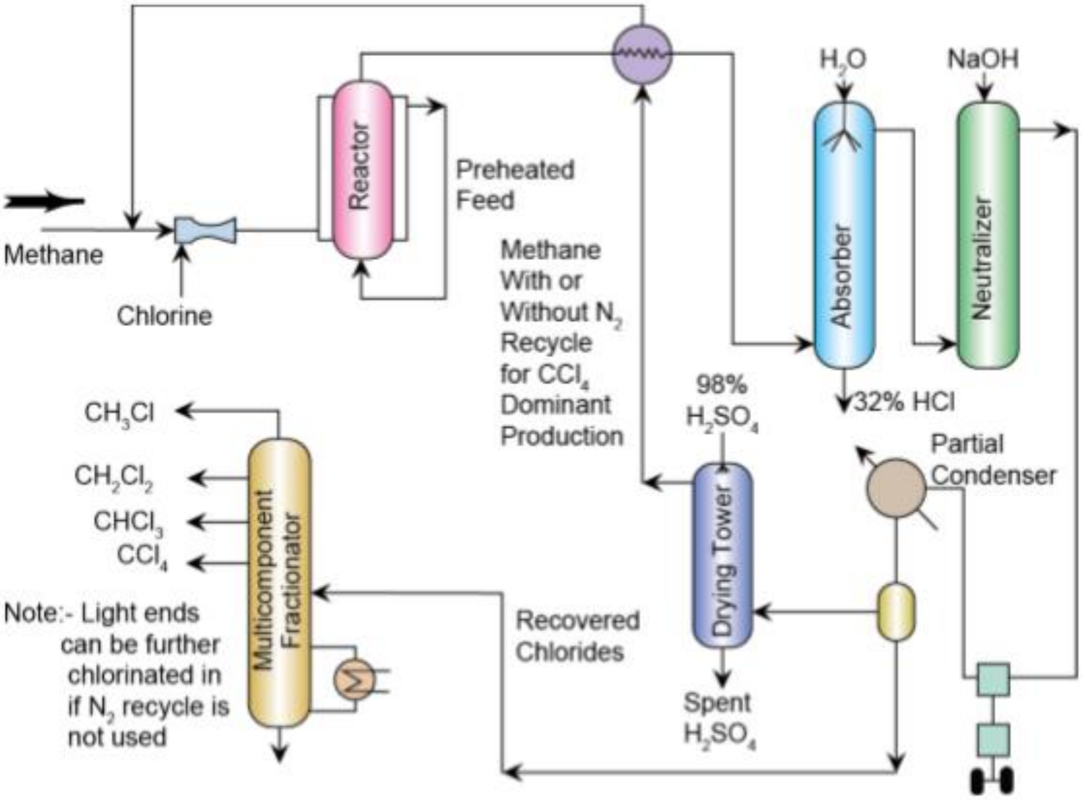
- The reactions are very exothermic.
- The feed molar ratio affects the product distribution. When CH4/Cl2 is about 1.8, then more CH3Cl is produced. On the other hand, when CH4 is chosen as a limiting reactant, more of CCl4 is produced. Therefore, depending upon the product demand, the feed ratio is adjusted.

Process Technology

- Methane and Cl2 are mixed and sent to a reactor
- The reactor has a jacket or shell and tube system to accommodate feed p reheating to desired furnace inlet temperature (about 280 – 300 ^{o}C).
- To control temperature, N_2 is used as a diluent at times.
- Depending on the product distribution desired, the CH4/Cl2 ratio is chosen.

- Eventually, the mixture enters an absorber where water is used as an absorbent and water absorbs the HCl to produce 32 % HCl.
- The trace amounts of HCl in the vapour phase are removed in a neutralizer fed with NaOH

- The gas eventually is compressed and sent to a partial condenser followed with a phase separator. The phase separator produces two streams namely a liquid stream consisting of the chlorides and the unreacted CH4/N2.
- The gaseous product enters a dryer to remove H2O from the vapour stream using 98% H2SO4 as the absorbent for water from the vapour.
- The chloromethanes enter a distillation sequence. The distillation sequence consists of columns that sequentially separate CH3Cl, CH2Cl2, CHCl3 and CCl4.



Flow sheet of Chloromethane production

Uses of Chloromethane :

1- The major use of methyl chloride is to produce silicon polymers.

2-Other uses include the synthesis of tetramethyl lead as a gasoline octane booster, a methylating agent in methyl cellulose production, a solvent, and a refrigerant.

3-Methylene chloride has a wide variety of markets. One major use is a paint remover.

4- It is also used as a degreasing solvent, a blowing agent for polyurethane foams, and a solvent for cellulose acetate.

Discussion

1. Why compressor is used before partial condenser?

Ans: The compressor increases the pressure of the system which is beneficial to increase the boiling points of the mixtures. Note that the boiling points of chloromethanes are -97.7, -97.6, -63.5 and -22.6 oC for CH3Cl, CH2Cl2, CHCl3 and CCl4 respectively. On the other hand, the boiling point is -161.6 oC. For these boiling point mixtures, when the system pressure is increased substantially, the boiling points of the compounds increase and could reach close to those of the cooling water (20 – 30 oC). Cooling water is required in the partial condenser and if it is not used, a refrigerant needs to be used which requires an additional refrigeration plant. Therefore, the system pressure is increased.

2. Why water is removed using the dryer?

Ans: Water enters the vapour system due in the absorption column where solvent loss to the vapour will be a common feature. Water molecule can react with the highly active intermediate chloromethanes to form oxychlorides, which are highly undesired.

3. Will there be any difficulty in separation by increasing boiling points of the chloromethane in the distillation sequences?

Ans: Definitely yes. This is because the relative volatility of compounds atleast slightly increases with reducing pressure and viceversa. But due to cooling water criteria in the distillation sequences also, there is no other way economical than doing distillation at higher pressure.

4. Since the boiling point of CH3Cl and CH2Cl2 are very close, what do you expect for the production of CH3Cl from the first column?

Ans: It is indeed difficult to separate CH3Cl and CH2Cl2 and therefore, good number of separation trays be used. Or structured packing be used to reduce the height of the first column.

5. When the reactions are highly exothermic, why is the feed pre-heated?

Ans: Irrespective of the reactions being exothermic or endothermic, the reaction rate always increases with temperature for non-equilibrium reactions. Therefore, feed is pre-heated to the desired temperature so as to fastly convert the reactants to products.

Lecture 9

Ethylene derivatives

Vinyl Chloride from Ethylene.

Introduction

- In this lecture we study the process technology involved in the **production of Vinyl Chloride from Ethylene**
- Vinyl chloride is produced in a two steps process from ethylene
  - Ethylene first reacts with Chlorine to produce Ethylene dichloride
  - The purified Ethylene dichloride undergoes selective cracking to form vinyl chloride
- We first present the process technology associated to Ethylene Chloride

5.1 Ethylene dichloride

5.1.1 Reactions

- $\mathbf{C2H4 + Cl2 \rightarrow C2H4Cl2}$
- Undesired products: Propylene dichloride and Polychloroethanes
- Reaction occurs in a liquid phase reactor with ethylene dichloride serving as the liquid medium and reactants reacting the liquid phase
- Catalyst is $FeCl_3$ or Ethylene dibromide

5.1.2 Process Technology (Figure 5.1)

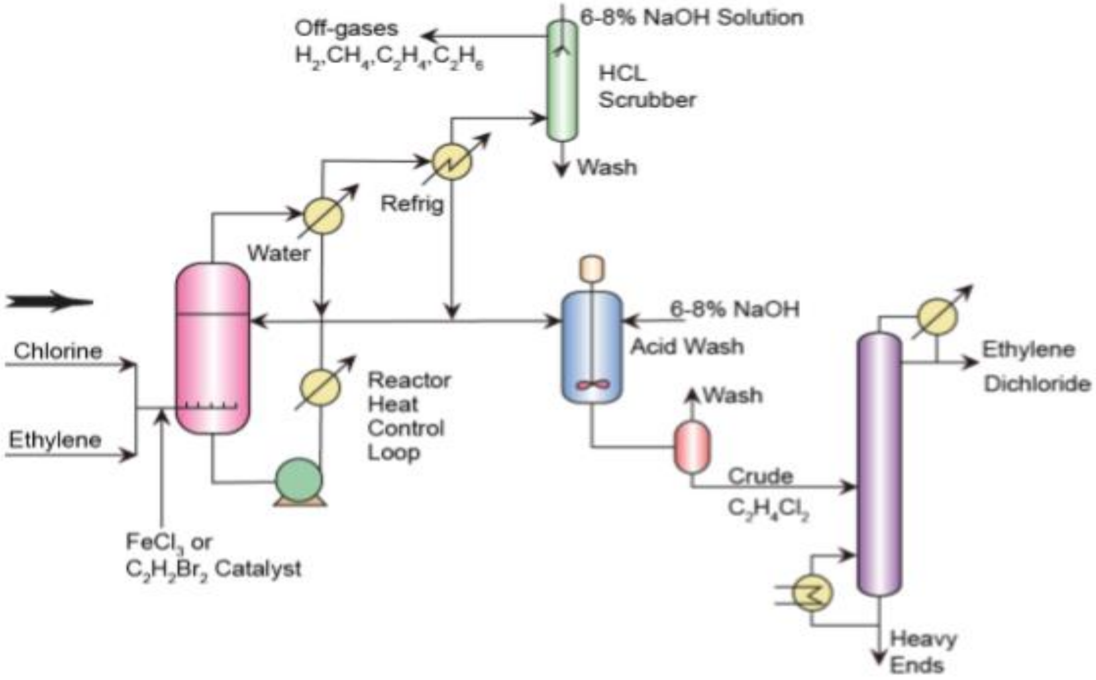


Figure 5.1 Flow sheet of production of ethylene dichloride

- C_2H_4 and Cl_2 are mixed and sent to the liquid phase reactor.
- Here, the feed mixture bubbles through the ethylene dichloride product medium Reactor operating conditions are 50 °C and 1.5 – 2 atms.
- The reaction is exothermic. Therefore, energy is removed using either cooling jacket or external heat exchanger
- To facilitate better conversion, circulating reactor designs are used.
- FeCl3 traces are also added to serve as catalyst
- The vapour products are cooled to produce two products namely a vapour product and a liquid product. The liquid product is partially recycled back to the reactor to maintain the liquid medium concentration.
- The vapour product is sent to **a refrigeration unit** for further cooling which will further extract ethylene dichloride to liquid phase and makes the vapour phase bereft of the product.

- The liquid product is crude ethylene dichloride with traces of HCl. Therefore, acid wash is carried out first with dilute NaOH to obtain crude ethylene dichloride. A settling tank is allowed to separate the spent NaOH solution and crude $C_2H_4Cl_2$ (as well liquid).
- The crude ethylene dichloride eventually enters a distillation column that separates the ethylene dichloride from the other heavy end products.
- The vapour phase stream is sent to a dilute NaOH solution to remove HCl and produce the spent NaOH solution. The off gases consist of H_2, CH_4, C_2H_4 and C_2H_6.

Discussion

1. Provide an insight into the liquid phase guided gas phase reaction?

Ans: The liquid phase acts as a resistance phase for the movement of various gases. The recirculator enables greater turbulence of the liquid phase stream. Thereby, using these mechanisms, the gases are allowed to react with one another and produce ethylene dichloride which gets dissolved in the liquid.

2. Why a water condenser followed by refrigeration is used when the single refrigeration can serve the purpose of cooling?

Ans: **This is an important question.** Allowing only refrigeration enhances process costs drastically. Therefore, water is used to carry out partial condensation and then refrigeration, even though in principle, water condensation can be bypassed and reactor operation and stream contacting can be further optimized.

3. Why do we need a settling tank after the acid wash unit associated to the crude ethylene dichloride?

Ans: Typically, we observe HCL removal from vapour streams. In such case, the unit used is a scrubber or absorber. The gas/vapour is fed to the absorption column and is obtained as a gas. When a liquid is allowed for scrubbing, it is possible to obtain emulsions of the organic phase in the aqueous phase. Therefore, provide gravity settling mechanism should exist so as to separate the crude ethylene dichloride from the mixture emanating from the acid wash tank.

5.2 Vinyl chloride production

5.2.1 Reaction

- $\mathrm{C2H4Cl2} \rightarrow \mathrm{CH2CHCl} + \mathrm{HCl}$
- Charcoal is used as the catalyst
- The reaction is a reversible gas phase reaction

5.2.2 Process Technology (Figure 5.2)

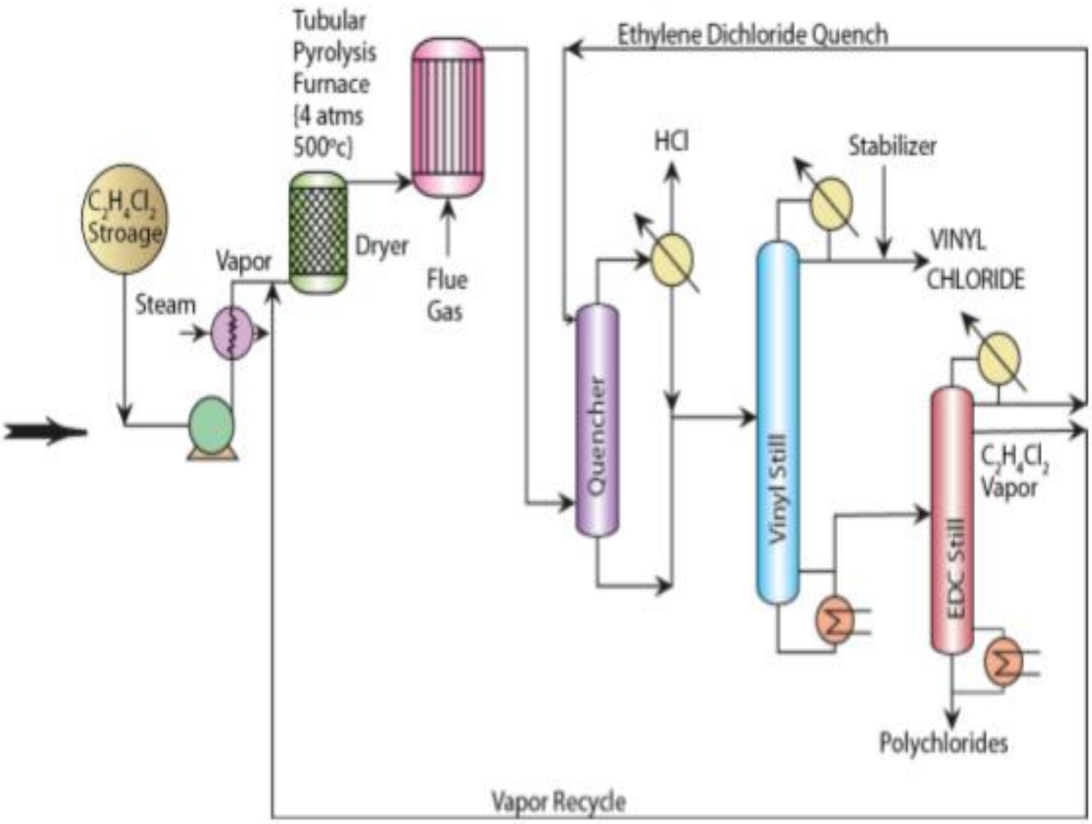


Figure 5.2 Flow sheet of production of vinyl chloride

- Ethylene dichloride is initially vaporized using a heat exchanger fed with process steam - Ethylene vapors then enter a dryer that removes traces of water molecules

- After drying, the vapors enter a pyrolysis furnace operated at 4 atm and 500 ^{o}C. The furnace is similar to a shell and tube arrangement with the gases entering the tube side and hot flue gas goes past the tubes in the shell side.
- The product vapors eventually enter a quenching tower in which cold ethylene dichloride is used to quench the product gases and cool them.
- The gases from the quench tower then enter a partial condenser which produces HCl as a gas and the liquid stream consisting of vinyl chloride, unreacted ethylene dichloride and polychlorides.
- The liquid stream from the quench tower as well as the condenser is fed to the vinyl still which produces the vinyl chloride product. The product is stabilized using a stabilizer as vinyl chloride is highly reactive without stabilizer.
- The bottom product from the vinyl still is fed to a distillation column which separates the ethylene dichloride from the polychlorides. The ethylene dichloride vapors are recycled back to the cracking furnace and the ethylene dichloride liquid is sent to the quenching tower to serve as the quenching liquid.

Discussion

1. Why ethylene dichloride is dried before entering the cracking furnace?

Ans: To avoid the formation of other compounds during cracking. Vinyl chloride cracking is a very selective cracking that we wish to happen. The selective cracking needs very clean feed stock.

2. Why quenching is carried out?

Ans: The selective cracking reaction is a reversible reaction. Therefore, by doing cold ethylene dichloride quenching, we are suppressing the backward reaction and ensuring that only vinyl chloride gets formed in good quantities.

3. Can heat integration be carried out in the process?

Ans: IN principle it can be done but in reality no. The reason is that if quenching is not done immediately, then vinyl chloride can get converted back to the ethylene dichloride. Therefore, though there is a hot stream available, heat integration cannot be done due to prevalent process conditions.

4. **Can a partial condenser be used in the last distillation column to serve for both quenching, distillation reflux and produce vapour for the ethylene dichloride?**

   Ans: Yes, this arrangement will be excellent as all requirements in the process will be met by going for a partial condenser. But it all depends on the quenching tower requirements and hence if ethylene dichloride needs to be cooled more than its boiling point, then partial condenser will not serve the purpose.

5. **What is the effect of pressure on quenching? This question is interesting as the reaction occurs at 4 atm and quenching occurs at higher pressure?**

   Ans: Quenching is an operation used for minimizing temperature. As such it’s not absorption where pressure plays an important role. As such, the effect of pressure will not be significant in the quenching operation.

Lecture 10

Ethylene derivatives

Ethylene oxide and Ethanol amines

6.1 Ethylene Oxide

6.1.1 Introduction

- In this lecture, we discuss upon the process technology for ethylene oxide and ethanol amines.
- Ethylene oxide is produced by the oxidation of ethylene using air
- Ethanol amines are produced using the series reaction scheme of ethylene oxide with ammonia.
- Ethanol amines are significantly used as absorbents to remove CO_2 and H_2S from process gas streams.

6.1.2 Ethylene Oxide

6.1.2.1 Reactions

- $C2H4 + O2 \rightarrow CH2O.CH2O$
- Ethylene to air ratio: 3 – 10 %
- Side reaction products: CO_2, H_2O
- Catalyst: Silver oxide on alumina
- Operating temperature and pressure: 250 – 300 °C and 120 – 300 psi
- Supressing agent for side reactions: Ethylene dichloride
- Reaction is exothermic

6.1.2.2 Process technology (Figure 6.1.1)

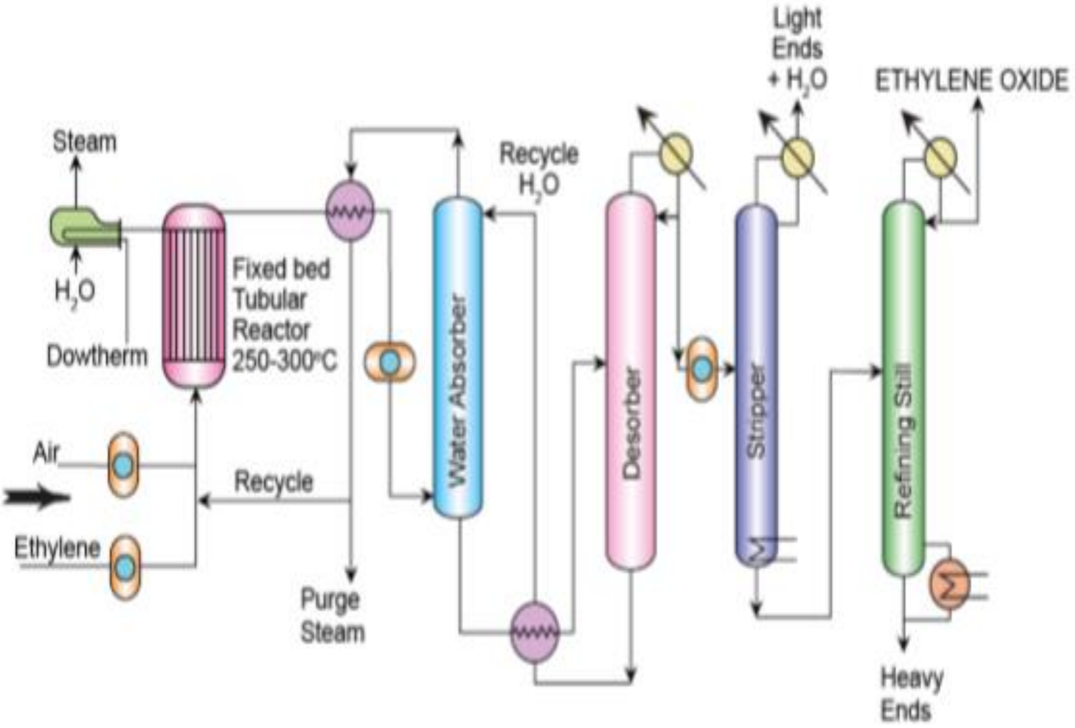


Figure 6.1.1 Flow sheet of production of ethylene oxide

❖ Air and ethylene are separate compressed and along with recycle stream are sent to the shell and tube reactor

❖ The reactor is fed on the shell side with Dowtherm fluid that serves to maintain the reaction temperature. A dowtherm fluid is a heat transfer fluid, which is a mixture of two very stable compounds, biphenyl and diphenyl oxide. The fluid is dyed clear to light yellow to aid in leak detection.

❖ - The hot dowtherm fluid from the reactor is sent to a waste heat recovery boiler to generate steam

❖ - The vapour stream is cooled using a integrated heat exchanger using the unreacted vapour stream generated from an absorber.

❖ - The vapour stream is then sent to the heat integrated exchanger and is then sent back to the reactor and a fraction of that is purged to eliminate the accumulation of inerts such as Nitrogen and Argon.

- - The product vapors are compressed and sent to a water absorber which absorbs ethylene oxide from the feed vapors. Eventually, the ethylene oxide rich water stream is sent to a stripper which desorbs the ethylene oxide + water as vapour and generates the regenerated water as bottom product. The regenerated water reaches the absorber through a heat integrated exchanger.
- - The ethylene oxide + water vapour mixture is compressed (to about 4 - 5 atms) and then sent to a stripper to generate light ends + H2O as a top product and the bottom product is then sent to another fractionators to produce ethylene oxide as top product. The heavy ends are obtained as bottom product.

Discussion

1. What is Dowtherm?

Ans: Dowtherm is an organic liquid that can attain to temperatures up to 300 ^{o}C. These are special fluids used instead of steam/water. In this example, the operating temperature is about 250 - 300 ^{o}C and therefore usage of Dowtherm fluid is perfect.

2. In what way compression is beneficial to the absorption?

Ans: It is a known fact that absorption is most favored at low temperature and high pressure. Therefore, compression of the cooled product gases will be very beneficial to maximize the dissolution of ethylene oxide in the water. Of course, along with ethylene oxide other light ends and heavy ends also dissolve in water and we have no control over that.

3. Why again another compressor is used before the stripper?

Ans.: The second compressor aids to enhance the boiling points of the mixtures. There by, water can be used as a cooling fluid in the distillation columns, as the boiling point of the products is enhanced by compression. In this regard, it should be noted that ethylene oxide has a boiling point of 10.7 ^{o}C which can be drastically enhanced by compression to 4 – 5 atms.

4. Why ethylene and air are separately compressed?

Ans.: This is due to the danger of generating an explosive mixture during compression step of the mixture.

5. What process modifications are possible for the flow sheet?

- Using a fluidized bed instead of packed bed reactor
- Using oxygen instead of air

6. Discuss the energy integration capacity of the process?

Ans.: In this process, the heat integration drastically reduced process steam requirements. Steam is only required in the strippers and fractionators. This steam can be generated using waste heat recovery units using dowtherm fluid as the hot fluid to generate the steam. Thus in this process, it is observed that for 1 ton of ethylene oxide produced, only 0.1 ton of steam is required. This is all possible due to significant heat integration in the process.

** 6.2 Ethanol amines**

6.2.1 Reactions

$$6\,\overset{O}{CH_2-CH_2} + 3\,NH_3 \longrightarrow H_2NCH_2CH_2OH + HN(CH_2CH_2OH)_2 + N(CH_2CH_2OH)_3$$

- ❖ The above reactions are series reaction scheme
- ❖ Reaction is exothermic
- ❖ Ammonia is in aqueous phase and ethylene oxide is in vapour state. Therefore, the reaction will be gas-liquid reaction
- ❖ Ethylene oxide is the limiting reactant.

6.2.2 Process technology (Figure 6.2)

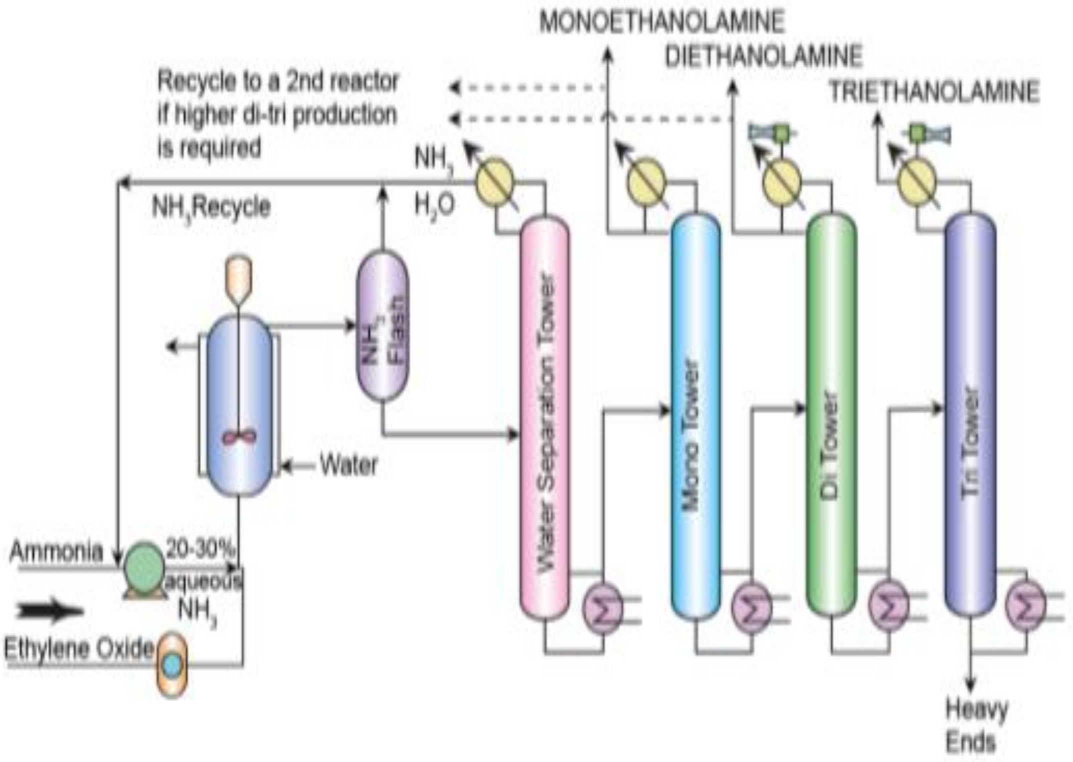


Figure 6.2 Flow sheet of production of ethanol amines

- Ammonia is mixed with ammonia recycle stream from the process and pumped to the CSTR where liquid phase ammonolysis takes place.
- Ethylene oxide is compressed and fed to the CSTR.
- The CSTR operating pressure will be such that the feed (and product) mixtures do not vaporize and good liquid phase reaction can occur.
- The reactor is cooled using water in the cooling jacket as the reactions are mildly exothermic
- The product stream is then sent to a flash unit that separates NH_3 + H_2O as a vapour stream and water + ethanol amines as a liquid stream.
- The ammonia + water stream is recycled to mix with the fresh ammonia and enter the reactor.
- The bottom product from ammonia flash unit is sent to a water separation tower that again removes dissolved ammonia in the ethanolamine rich solution. Once again ammonia + water are generated and this stream is also recycled to mix with fresh ammonia feed.
- The bottom product consisting of crude mixture of ethanol amines and heavy ends.
- This mixture is fed to a mono ethanol amine tower first to separate the mono ethanol amine from the other two and heavy ends
- The bottom product from the first distillation tower then enters the second and third distillation towers which are operated under vacuum to produce di ethanol amine and tri ethanol amine as top products. The bottom product from the last distillation tower is the heavy ends product.

Discussion

1. In what way operating the CSTR In liquid phase is beneficial?

Ans.: Liquids have higher mass transfer coefficients than solids. Therefore, if the reaction needs be facilitated with two components, if they are in liquid phases, then reactions could be faster. Therefore, pressure can play an important role in both altering the selectivity as well as conversion of the series reactions scheme.

2. Why ammonia + water needs to be separated from the second tower i.e., water separation tower?

Ans.: Ammonia dissolves instantaneously in water to form ammonia solution. This chemical affinity of ammonia is very difficult to get it through. On the other hand, despite using flash unit, some ammonia will remain the water consisting of ethanol amines and heavy ends. Therefore, the second water separation tower is required to remove once again ammonia + water from the solution.

3. Why vacuum is used in the second and third distillation towers?

Ans.: The di ethanol and tri ethanol amines dissociate at high operating temperatures. Therefore, vacuum is used to reduce the operating temperature of the distillation columns (second and third).

4. What process modifications you can suggest for better operation?

Ans.: When higher quantities of di or tri ethanol amine is desired, then the mono ethanol amine can be sent to another reactor in which ethylene oxide is added. It's not advisable to recycle it the CSTR shown in the process flow sheet as it can form amino-ethers but not di ethanolamine.

5. Can solvents (extraction) be used instead of vacuum distillation for the separation of di and tri ethanol amines?

Ans.: No, this is due to the reason that solvents tend to have similar solubility factors for both di and tri ethanol amines.

Lecture 11

Propylene derivatives

Isopropanol and Acetone from Propylene

Introduction

- In this lecture we study the process technology associated to the manufacture of isopropanol and acetone.
- Isoprpanol is manufactured from hydration of **propylene**
- Acetone is produced using the dehydrogenation route of isopropanol
- We first present the isopropanol process technology

7.1 Isopropanol manufacture

7.1.1 Reaction

- ➢ Sulfation: $CH_3CHCH_2 + H_2SO_4 \rightarrow (CH_3)_2\,\mathrm{CH}(OSO_3\mathrm{H})$Isopropyl acid sulphate)
- ➢ Hydrolysis: Isopropyl sulphate $+ H_2O \rightarrow$ Isopropanol + Sulfuric acid

Thus sulphuric acid is regenerated in the process

- ➢ Side reaction: Diisopropyl sulphate $+ H_2O \rightarrow$ Diisopropyl ether + Sulfuric acid
- ➢ Therefore, the primary reaction is a gas liquid reaction in which propylene is absorbed into a tray tower fed with sulphuric acid.
- ➢ Operating conditions: Room temperature but 20 – 25 atms pressure
- ➢ Reaction is highly exothermic

7.1.2 Process technology (Figure 7.1)

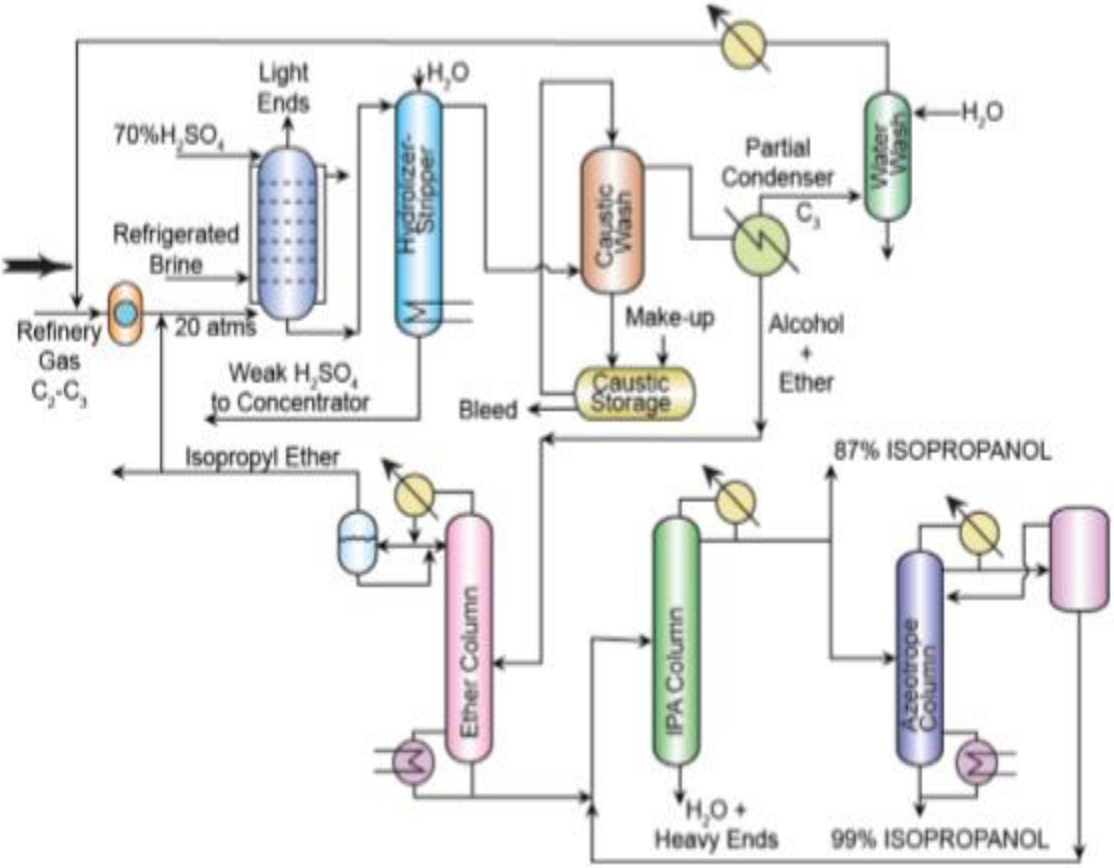


Figure 7.1 Flow sheet of Isopropanol manufacture

- Either pure propylene or a mixture of Propylene and other C_2, C_3 components can be fed to a reactor.
- The hydrocarbon feed is compressed and fed to the reactor at about 20 – 25 atms pressure.
- Sulphuric acid of about 70% acid strength is fed in a countercurrent mode to the tray column where reactive absorption takes place. Here, sulfonation reaction takes place.
- The reaction is highly exothermic and therefore, refrigerated brine is used to control the temperature in the absorber. Jacketed arrangement will be preferred for the tray absorption column to circulate the refrigerated brine in the cooling jacket.

- After reaction, the unreacted light ends such as saturated components will leave the unit as the gas stream.
- The sulfonated product rich stream is then sent to a hydrolyzer cum stripper where isopropanol is produced and is vaporized due to existing stripper temperatures.
- The hydrolyzer is fed with water to facilitate the conversion of the sulfonate product.
- The isopropanol rich vapors then enter a caustic wash unit to remove the acidic impurities. - The isopropanol rich vapors then enter a partial condenser which separates the unreacted propylene from the alcohol + ether mixture. Here, propylene is separated as the vapour and alcohol + ether is separated as the liquid stream.
- The separated propylene gas is once again subjected to water wash to remove soluble impurities (such as ethers and alcohols). Subsequently, pure propylene is sent to mix with the fresh feed stream. Before sending to the unit, the propylene is cooled to room temperature so as to have identification conditions as the fresh feed stock.
- The alcohol and ether enter a ether column that separates isopropyl ether which is returned to the reactor.
- The bottom product consisting of isopropyl alcohol and water is sent to a isopropyl alcohol column that produces water + heavy ends as the bottom product and 87 % isoprpanol-water azeotrope mixture as the top product.
- The azeotrope is sent to an azeotropic distillation column that uses isopropyl ether as a azeotropic agent to obtain 99 % isopropanol as the bottom product. The top product is a mixture of isopropyl ether and water. The top product is a low boiling azeotrope. This stream upon gravity settling will produce the isopropyl ether as the top product which is sent as a reflux stream to the azeotropic column. The bottom product is a mixture of isopropanol and water is recycled back to the isopropyl alcohol column along with the bottom product generated from the ether separating column.

7.1.3 Uses of Isopropanol:

There may be many uses of iso-propanol, industrial as well as common uses. It finds use in pharmaceutical applications because of the low toxicity of any residues. Isopropanol is also used as a chemical intermediate in some industrial processes. It is also used as a gasoline additive.

Discussion

1. Why refrigerated brine is used in the sulfonation reactor?

Ans.: The reaction temperature is room temperature (25 – 30 ^{o}C). Therefore, refrigerated fluid is used. Brine is used here, as refrigerated is antifreeze and can allow solution to reach lower temperatures without freezing problem.

2. Why a partial condenser but not total condenser is used to separate C_3 from alcohol + ether?

Ans.: Apart from costs, the total condenser produces a single stream and this is of no use as propylene must be separated and sent as a gas back to the sulfonation reactor. All this is achieved in a single process unit by using partial condensation principle.

3. Why is isopropyl ether circulated back to the sulfonation reactor?

Ans.: To suppress the side reaction and hence decomposition of sulfonation to less valued product.

4. Present the working principle of an azeotropic distillation column?

Ans.: The azeotropic distillation column is fed with the azeotrope mixture and another component which forms a low boiling heterogenous azeotrope with the feed (azetropic mixture) components as one of the products and a purer compound as the other product. The low boiling azeotrope is then sent to a gravity settler that separates the heterogeneous phases into two products namely the azeotropic agent and an impure mixture of the original components. The impure mixture is actually fed to one of the distillation columns in the process flow sheet at a location that matches with the purity of the stream.

5. What happens to the water in which acid gets dissolved in the hydrolyzer cum stripper column?

Ans.: Here, the stream is a weak acid stream that is fed to a multiple effect evaporator to concentrate the weak acid solution to a strong acid solution. The strong acid solution then can be used as one of the raw materials in the process.

6. Can you do heat integration for the partial condenser with the sulfonation reactor?

Ans.: No, the reason is that sulfonation reaction is highly exothermic and heat needs to be quickly removed. This is not possible when vapors are used as the cooling stream as gas phase heat transfer coefficients are significantly lower than the liquid phase heat transfer coefficients.

7. Can a partial condenser be used for the ether column?

Ans.: Yes, the reason is that there is no hard and fast rule that isopropyl ether be added in the liquid phase to the sulfonation reactor. In fact, it should be added as a vapour phase only and therefore, partial condenser should be used in place of total condenser to save costs as well as meet the process specifications.

7.2 Acetone manufacture from isopropanol

7.2.1 Reactions

- Dehydrogenation of Isopropanol
- Isopropanol → Acetone + H2
- Reaction pressure: 3 – 4 atms
- Reaction temperature: 400 – 500 °C
- Copper catalyst on porous carrier is used
- Vapor phase reaction

7.2.2 Process Technology (Figure 7.2)

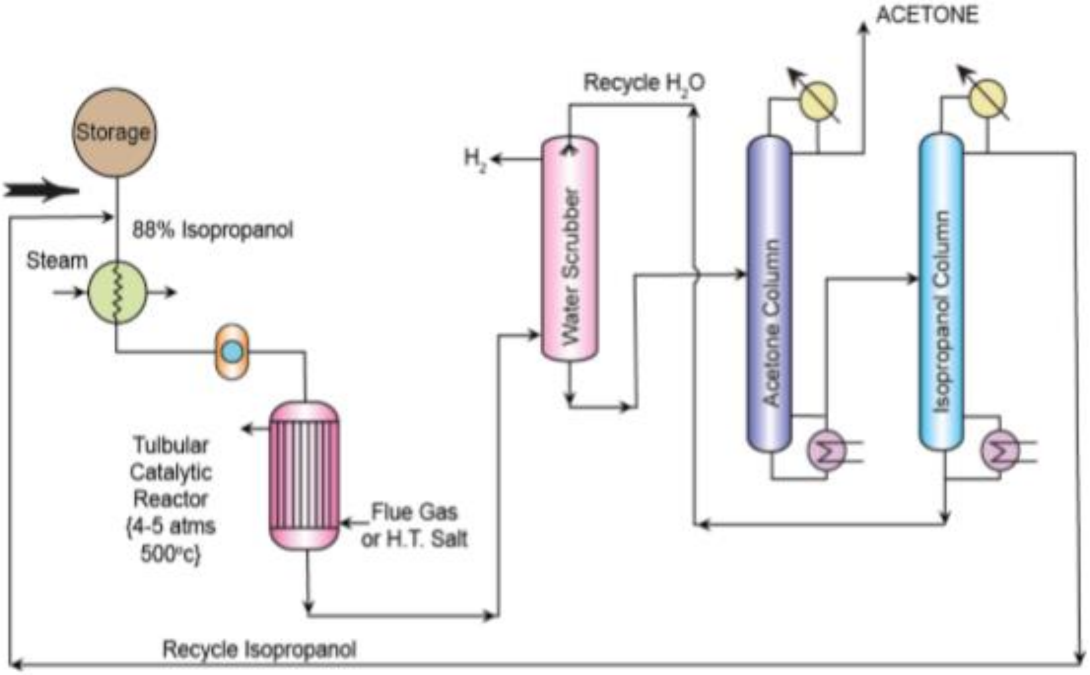


Figure 7.2 Flow sheet of acetone manufacture from isopropanol

- First, Isopropanol is heated using steam to vaporize the same.
- Then, Isopropanol is compressed to desired reactor pressure i.e., 4 – 5 atms
- The compressed Isopropanol then enters a catalytic shell and tube reactor in the tube side. The tube is packed with the porous copper catalyst

- The reactor is operated at 400 – 500 °C using flue gas for heating. The flue gas is passed in the shell side of the shell and tube reactor.
- After reaction, the gases are condensed using cooling water condenser. The condensed isopropanol and acetone are sent for fractionation.
- The gases consisting of the remaining quantities of isopropanol and acetone are absorbed into water using a water scrubber.
- The acetone + isopropanol obtained from the condenser and water + isopropanol + acetone are sent to an acetone fractionator that separates acetone as the top product and isopropanol + water as bottom product.
- The bottom product isopropanol + water from the acetone fractionators is sent to a isopropanol column.
- This column produces water as the bottom product and isopropanol as the top product.
- The water is cooled using a water condenser and sent to the water scrubber as fresh water solvent.

7.2.3 Uses of Acetone:

**Acetone is used as a polar, aprotic solvent in a variety of organic reactions. One important property for which it is used as laboratory solvent is because does not form an azeotrope with water.

**Acetone is also used in various medical and cosmetic applications. It also forms an important component in food additives and food packaging.

Discussion

1. **Is pure isopropanol required as feedstock in the reactor?**

Ans: This question is asked due to the fact that isopropanol production process involves the formation of an azeotrope with 87 % Isopropanol and 13 % water. Therefore, if the azeotrope itself can be used as feedstock, then one can save azeotropic column costs if an acetone plant is constructed next to the isopropanol.

Yes, isopropanol azeotrope can be used as a feed stock. In this case, the water will not react and will condense in the condenser after the reactor.

2. **Can’t we feed the product gases directly to the water absorber eliminating the condenser?**

   Ans: The condenser removes the condensable components from the product vapors. If condenser is not used, then the hot vapors move to the absorber and absorber load and degree of separation should be pretty high and hence higher cost. Therefore, it’s better to use the water cooling condenser.

3. **Why is water from the isopropanol fractionators cooled and sent to the water absorber unit?**

   Ans: This is due to the fact that absorption is favored at lower temperature and higher pressure.

4. **Why are isopropanol again sent to the compressor along with the feed?**

   Ans.: The operating pressures of the absorber, acetone fractionator and isopropanol fractionators reduce sequentially as the stream progresses to the right side. Therefore, the last column produces the product with about atmospheric pressure only. Therefore, to bring it back to 5 atm as in the reactor conditions, the stream has to be compressed along with the feed stream.

Lecture 12

Propylene derivatives

Cumene and Acrylonitrile from Propylene

Introduction

- In this lecture, we study the process technology associated to the production of cumene and acrylonitrile from propylene
- Both Cumene and Acrylonitrile are very important compounds that are required for the manufacture of other downstream petrochemicals
- We first present the process technology associated to the Cumene

8.1 Cumene

8.1.1 Reactions

$$C_3H_6 \quad + \quad C_6H_6 \quad \rightarrow \quad C_6H_5\text{-}C_3H_7$$

- The reaction is exothermic

- Catalyst: H_3PO_4 impregnated catalyst on porous carrier
- Operating conditions: 25 atms pressure and 250 ^{o}C temperature.

8.1.2 Process technology (Figure 9 .1)

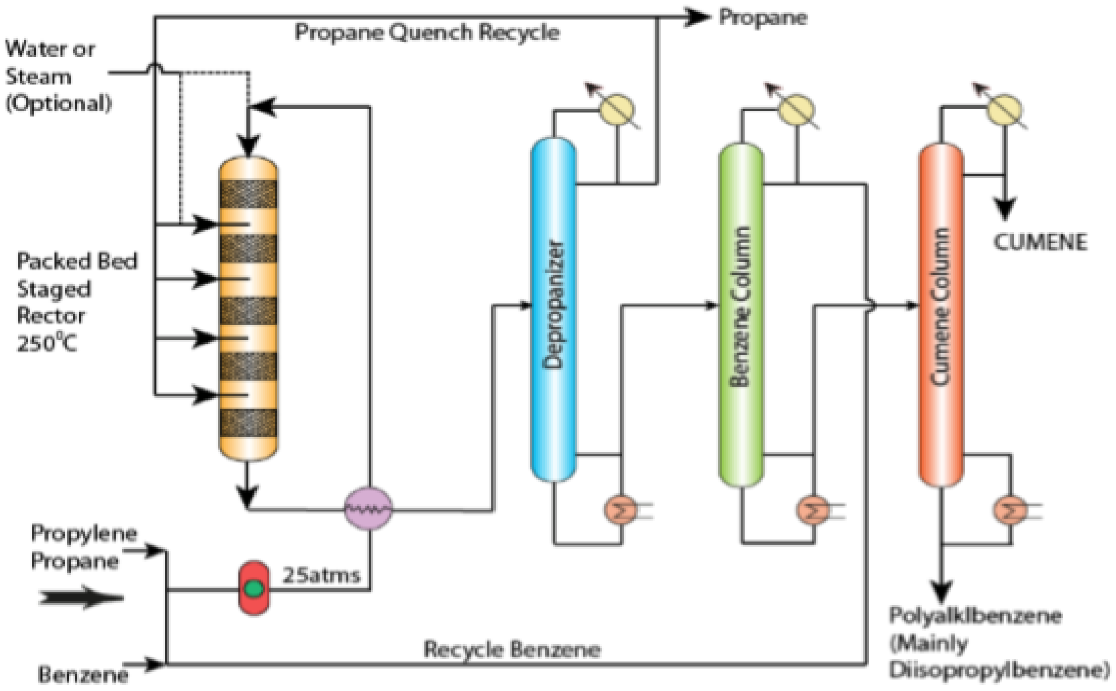


Figure 8.1 Flow sheet of Cumene production

- Propylene obtained from refinery processes as a mixture of propylene and propane
- The mixture along with benzene is compressed to 25 atms
- Eventually the mixture enters a heat integrated exchanger to heat the pre-heat the feed mixture.
- The feed mixture enters a packed bed reactor.
- The stream distribution in the packed bed reactor corresponds to cold shot arrangement i.e., cold propane from the distillation column in the process is added after every reactor with the product stream so that the temperature of the stream is controlled.
- Here, propylene is the limiting reactant and therefore, presumably all propylene undergoes conversion.
- Here, propane does not react but is a diluents or inert in the system. In that way it controls the reaction temperature.
- The reactor units are maintained at about 250 ^{o}C
- The product vapors are cooled using the heat integrated exchanger
- The vapors then pass to a depropanizer which separates propane from the product mixture.
- The bottom product consisting of benzene, cumene and polyalkyl benzenes enters another distillation column which separates benzene from the mixture of cumene and polyalkyl benzene. The benzene stream is recycled to enter the compressor.
- The bottom product from the benzene column is sent to a cumene column which produces cumene as top product and poly alkyl benzene as bottom product.

Discussion

1. What alternative reactor arrangement is possible if pure propylene feed is used?

Ans.: When pure propylene is used, then there is no propane for quenching. Therefore, the packed bed reactor shall be provided a cooling jacket which can control the temperature of the reactor.

2. Comment on the sequence of distillation columns separating propane, benzene and cumene in series?

Ans.: The distillation columns are so arranged so that lighter components are separated first followed by heavier components. Since no component is present which will decompose on long time heating, this arrangement is followed. If not, the component which can decompose upon long time heating will be separated first following by the lighter to heavier component sequence in the remaining components.

3. In what way propane quenching plays a role in the reactions?

Ans.: Propane quenching reduces polymerization of cumene and formation of polyalkyl benzenes.

4. How can one suppress polyalkylbenzene formation?

Ans.: By using high feed ratio of benzene to propylene and using propane as a diluent

5. Is further heat integration not possible?

Ans..: A further heat integration can be carried out using hot vapors in the distillation column to be as hot streams in the re boilers of various distillation columns.

6. In what way higher pressure in the product vapors from the reactor are beneficial for the deprpopanizer unit?

Ans..: The depropanizer unit requires condensation of propane vapors in the condenser. Propane's boiling point is less than 0 ^{o}C at 1 atm pressure. Therefore, higher pressures to the extent of 25 atms will enhance propane boiling point to about 25 – 30oC for which cooling water can be used as the cooling media in the condenser. If not, refrigerant needs to be used and the refrigerant will require a refrigerating unit along with the process. This is much expensive than using cooling water as the cooling media.

8.2 Acrylonitrile

8.2.1 Reactions

- C3H6 + NH3 + O2 → C3H3N + H2O
- The reaction is exothermic
- Stoichiometric ratio: C3H6 : NH3 : O2 = 1:1:1.5
- Operating conditions: 1.5 – 3 atms pressure and 400 – 500 ^{o}C
- By products: Acetonitrile and Hydrogen cyanide from side reactions
- Catalyst: Mo-Bi catalyst

8.2.2 Process Technology (Figure 8.2)

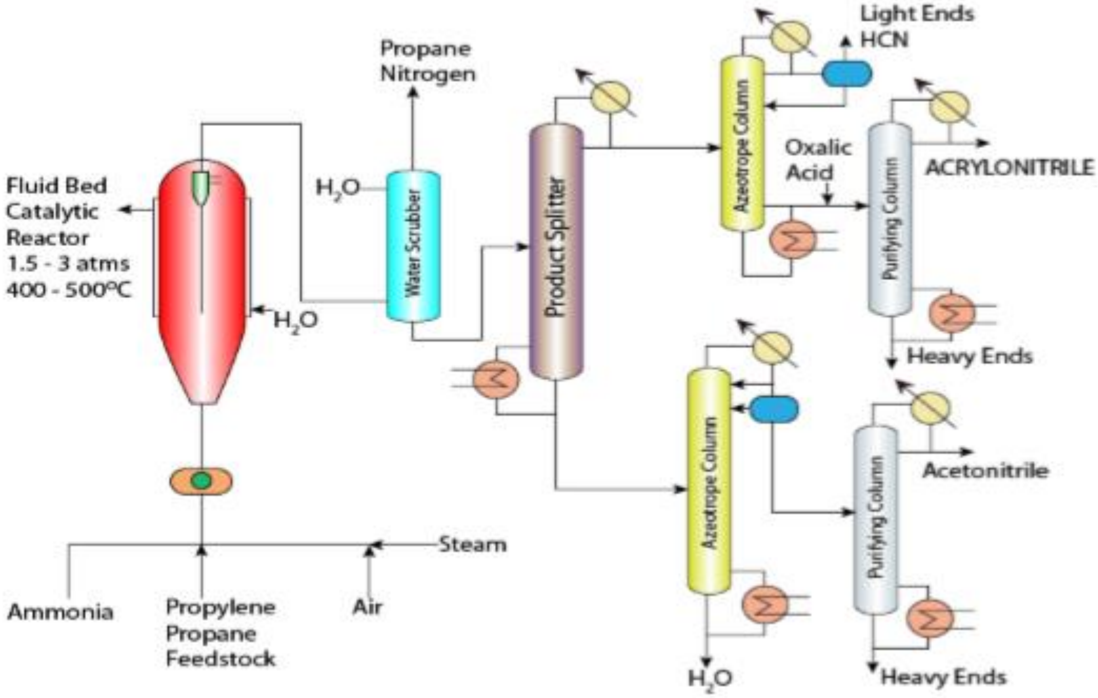


Figure 8.2 Flow sheet of Acrylonitrile production

❖ Propylene + Propane, Air and Ammonia, Steam are compressed to required pressure and are sent to the fluidized catalytic reactor consisting of the Mo-Bi spherical catalyst. The reactor is maintained at 400 – 500^{o}C.

- Cyclone separator is also kept in the fluidized bed reactor in which catalyst and product gases are separated after fludization. The contact time for fluidization is in the order of seconds.
- The product vapors then enter a water scrubber that does not absorb propane and nitrogen from the products. The products absorbed in the water include acrylonitrile, acetonitrile and other heavy ends.
- The very dilute acryolonitrile (about 3 %) solution in water is sent to a fractionator. The fractionators separates acrylonitrile + heavy ends + HCN + light ends as a top product stream and acetonitrile + water + heavy ends as a bottom product.
- The top product then enters an extractive distillation column with water as extractant. The azeotropic distillation column vapour is partially condensed to obtain a vapour, aqueous and organic layer. The vapour consists of Light ends and HCN and is let out. The organic layer consists of acrylonitrile and heavy ends is sent for further purification. The aqueous layer is sent as a reflux to the azeotropic column. In other words, addition of water enabled the formation of a heterogeneous azeotropic mixture at the top.
- The bottom product from the azeotropic distillation column enters a product purification unit along with oxalic acid where acrylonitrile is further purified from heavy ends (+ oxalic acid) and is obtained as a 99.5 % pure product.
- In similarity to this, the bottom product from the product splitter enters an azeotropic column which produces water as a bottom product. The total condenser in this column generates both aqueous and organic layers. The organic layer is rich in acetonitrile and heavy ends where as the aqueous layer is sent back as a reflux to the azeotropic column.
- The bottom product from the acetonitrile azeotropic column enters a purification unit where distillation principle enables the separation of acetonitrile from the heavy ends.

Discussion

1. Why is oxalic acid added in the acrylonitrile purification column?

Ans: One of the byproducts of the ammonoxidation of propylene are cyanohydrins.These organic compounds readily dissociate to form volatile compounds. These volatile compounds are severely polluting compounds. Therefore, to avoid this, oxalic acid is added to the purification column in order to form complex compounds with these cyanohydrins and these compounds eventually enter the heavy end products.

2. A careful analysis of the process flowsheet shown indicates that while absorption is favoured at lower temperatures and higher pressures, exactly opposite conditions exist for the reactor outlet stream (at about 1 atm pressure and 400 – 500oC). What additional process modifications are suggested?

Ans: Cooling the vapour product stream from 400 ^{o}C to about 50 ^{o}C in a series of heat exchangers. Since vapour is involved, extended area exchangers will be beneficial. Heat integration with the reboilers of any of the distillation columns is also beneficial.

Pressurizing the vapour pressure to higher pressure and allowing it to enter the scrubber at the same temperature. This is beneficial but compressor costs will be enormous.

Therefore, in the light of the process costs, cooling the vapour stream is beneficial than compression to favour good absorption.

3. In certain processes for acrylonitrile production, cyanohydrins removal is desired. If so, what process modifications are suggested?

Ans: Cyanohydrins are in the bottom product obtained in the product splitter. Therefore, the bottom product can be sent to a reactor where cyanohydrins can be converted to acrolein and these acroleins can be separated and sent back to the ammonoxidation reactor (fluidized beds). In that case, oxalic acids are not used and the heavy ends will not also get produced significantly and therefore process topology will be somewhat different from what is being shown here. For further details upon how the process flowsheet changes please refer to Chemical Engineering Design (Book) by Sinnott where in Appendix these modifications have been explained thoroughly in the process description.

4. Is a partial condenser required in the acetonitrile azeotropic column?

Ans: No, the reason is that the bottom product from the product splitter consists of heavy ends, acetonitrile and water and does not consist of lighter ends and HCN. Therefore, a partial condenser is not required and a total condenser producing two separate liquid phase streams that separate upon gravity is required.

5. A feed stock heater is not shown in the process. However, reactor operating conditions are indicate high temperature operation. How is the feed stock heated?

Ans: The heat for achieving the feed to desired temperature is provided by superheated steam that is mixed along with the feedstock. Typical feed molar composition is propylene 7, ammonia 8, steam 20 and air 65. Additional heat for the reaction is obtained from the highly exothermic reaction in the fluidized bed catalytic reactor.

6. What are the advantages of the fluidized catalytic reactor when compared to a packed bed reactor?

Ans: It is well known that the heat and mass transfer coefficients of gases are predominantly lower than those of the liquids. Therefore, fluidization principle effectively enhances bulk phase mass and heat transfer coefficients of the gas solid catalytic reaction. In other words, due to fluidization, less contact time that is required in the process, higher conversions can be achieved.

Lecture 13

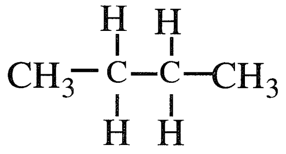
Petrochemical from n.paraffins

n-BUTANE CHEMICALS

Like propane, n-butane is mainly obtained from natural gas liquids. It is also a by-product from different refinery operations. Currently, the major use of n-butane is to control the vapor pressure of product gasoline. Due to new regulations restricting the vapor pressure of gasolines, this use is expected to be substantially reduced. Surplus n-butane could be isomerized to isobutane, which is currently in high demand for producing isobutene. Isobutene is a precursor for methyl and ethyl tertiary butyl ethers, which are important octane number boosters.[6] Another alternative outlet for surplus n-butane is its oxidation to maleic anhydride. Almost all new maleic anhydride processes are based on butane oxidation.

n-Butane has been the main feedstock for the production of butadiene. However, this process has been replaced by steam cracking hydrocarbons, which produce considerable amounts of by-product butadiene.

The chemistry of n-butane is more varied than that of propane, partly because n-butane has four secondary hydrogen atoms available for substitution and three carbon-carbon bonds that can be cracked at high temperatures:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ CH_3 & - & C & - & C & - & CH_3 \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Like propane, the noncatalytic oxidation of butane yields a variety of products including organic acids, alcohols, aldehydes, ketones, and olefins. Although the noncatalytic oxidation of butane produces mainly aldehydes and alcohols, the catalyzed oxidation yields predominantly acids.

OXIDATION OF n-BUTANE (Acetic Acid and Acetaldehyde)

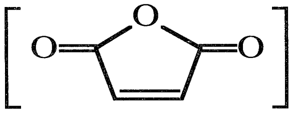
The oxidation of n-butane represents a good example illustrating the effect of a catalyst on the selectivity for a certain product. The noncatalytic oxidation of n-butane is nonselective and produces a mixture of oxygenated compounds including formaldehyde, acetic acid, acetone, and alcohols. Typical weight % yields when n-butane is oxidized in the vapor phase at a temperature range of 360–450°C and approximately 7 atmospheres are: formaldehyde 33%, acetaldehyde 31%, methanol 20%, acetone 4%, and mixed solvents 12%.

On the other hand, the catalytic oxidation of a n-butane, using either cobalt or manganese acetate, produces acetic acid at 75–80% yield. Byproducts of commercial value are obtained in variable amounts. In the Celanese process, the oxidation reaction is performed at a temperature range of 150–225°C and a pressure of approximately 55 atmospheres.[7]

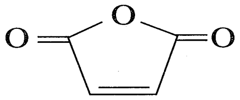
$$CH_3CH_2CH_2CH_3 + O_2 \rightarrow CH_3COOH + \text{by-products} + H_2O$$

The main by-products are formic acid, ethanol, methanol, acetaldehyde, acetone, and methylethyl ketone (MEK). When manganese acetate is used as a catalyst, more formic acid (≈25%) is obtained at the expense of acetic acid.

Maleic Anhydride:



Catalytic oxidation of n-butane at 490° over a cerium chloride, Co-Mo oxide catalyst produces maleic anyhydride:

$2\ CH_3CH_2CH_2CH_3 + 7\ O_2 \rightarrow 2$  $+ 8H_2O$

Other catalyst systems such as iron V_2O_5-P_2O_5 over silica alumina are used for the oxidation. In the Monsanto process (Figure 6-4), n-butane and air are fed to a multitube fixed-bed reactor, which is cooled with molten salt. The catalyst used is a proprietary modified vanadium oxide. The exit gas stream is cooled, and crude maleic anhydride is absorbed then recovered from the solvent in the stripper. Maleic anhydride is further purified using a proprietary solvent purification system.[8]

A new process for the partial oxidation of n-butane to maleic anhydride was developed by DuPont. The important feature of this process is the use of a circulating fluidized bed-reactor. Solids flux in the rizer-reactor is high and the superficial gas velocities are also high, which encounters short residence times usually in seconds. The developed catalyst for this process is based on vanadium phosphorous oxides

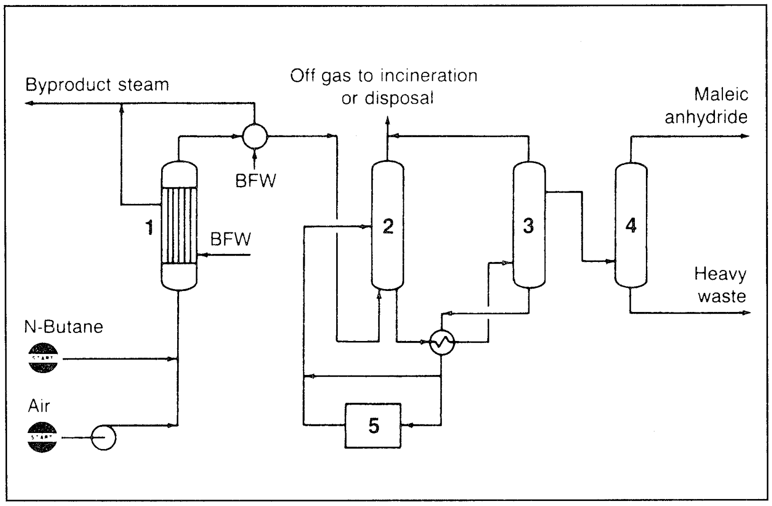


Figure 6-4. The Monsanto process for producing maleic anhydride from butane:[8] (1) reactor, (2) absorber (3) stripper, (4) fractionator, (5) solvent purification.

$(VO)_2P_2O_7$ type, which provides the oxygen needed for oxidation. The selective oxidation of n-butane to maleic anhydride involves a redox mechanism where the removal of eight hydrogen atoms as water and the insertion of three oxygen atoms into the butane molecule occurs. The reaction temperature is approximately 500°C. Subsequent hydrogenation of maleic anhydride produces tetrahydrofuran.[9] Figure 6-5 shows the DuPont butane to maleic anhydride process.

Oxidation of n-butane to maleic anhydride is becoming a major source for this important chemical. Maleic anhydride could also be produced by the catalytic oxidation of n-butenes (Chapter 9) and benzene (Chapter 10). The principal use of maleic anhydride is in the synthesis of unsaturated polyester resins. These resins are used to fabricate glass-fiber reinforced materials. Other uses include fumaric acid, alkyd resins, and pesticides. Maleic acid esters are important plasticizers and lubricants. Maleic anhydride could also be a precursor for 1,4-butanediol (Chapter 9).

Aromatics Production

Liquefied petroleum gas (LPG), a mixture of propane and butanes, is catalytically reacted to produce an aromatic-rich product. The first step is

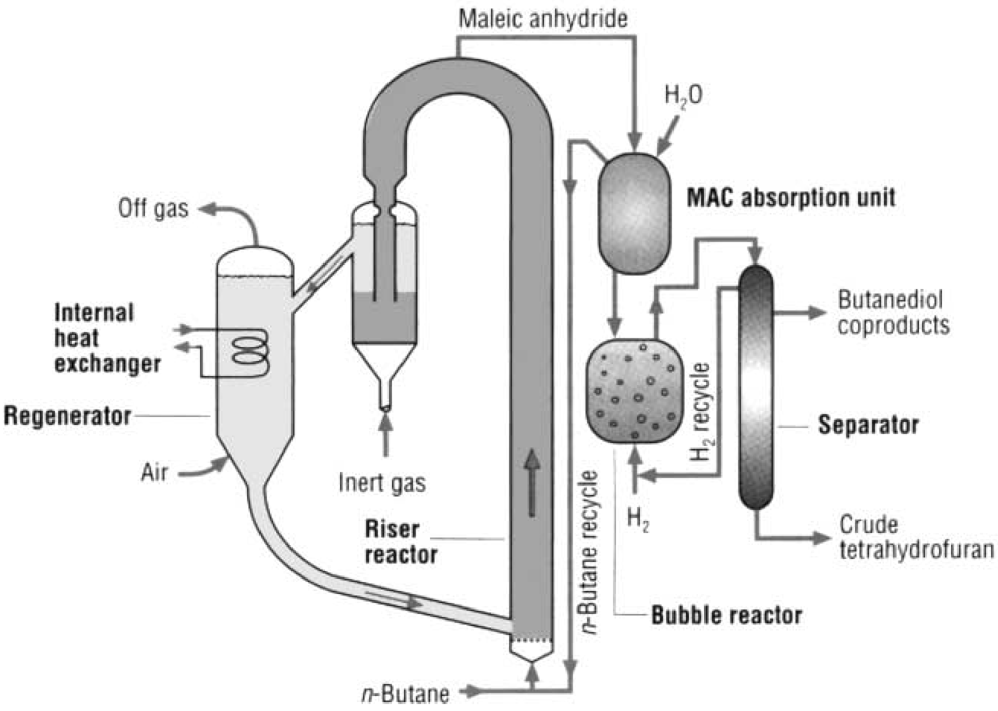
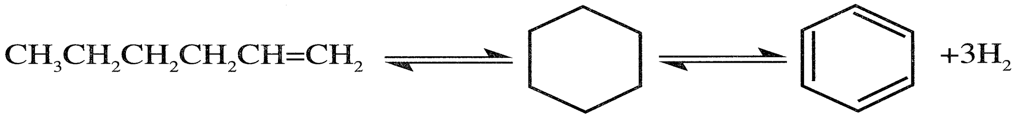


Figure 6-5. The DuPont butane to maleic anhydride process.[9]

assumed to be the dehydrogenation of propane and butane to the corresponding olefins followed by oligomerization to C_6, C_7, and C_8 olefins. These compounds then dehydrocyclize to BTX aromatics. The following reaction sequence illustrates the formation of benzene from 2 propane molecules:

$$2CH_3CH_2CH_3 \rightarrow \underset{\text{1-Hexene}}{CH_3CH_2CH_2CH_2CH{=}CH_2} + 2H_2$$



Although olefins are intermediates in this reaction, the final product contains a very low olefin concentration. The overall reaction is endothermic due to the predominance of dehydrogenation and cracking. Methane and ethane are by-products from the cracking reaction. Table 6-1 shows the product yields obtained from the Cyclar process developed jointly by British Petroleum and UOP.[10] A simplified flow scheme for the Cyclar process is shown in Figure 6-6.

The process consists of a reactor section, continuous catalyst regeneration unit (CCR), and product recovery section. Stacked radial-flow reactors are used to minimize pressure drop and to facilitate catalyst recirculation to and from the CCR. The reactor feed consists solely of LPG plus the recycle of unconverted feed components; no hydrogen is recycled. The liquid product contains about 92 wt% benzene, toluene, and xylenes (BTX) (Figure 6-7), with a balance of C_9^+ aromatics and a low nonaromatic content.[10] Therefore, the product could be used directly for the recovery of benzene by fractional distillation (without the extraction step needed in catalytic reforming).

Table 6-1
Product yield from saturated LPG feed to the cyclar process[10]

	Yields, wt% of fresh feed		
Feedstock	**Aromatics**	**Hydrogen**	**Fuel gas**
Propane (100%)	63.1	5.9	31.0
Butanes (100%)	65.9	5.2	28.9

Basis: High-yield mode. Lower cost Cyclar units can be designed, but for lower overall yields.

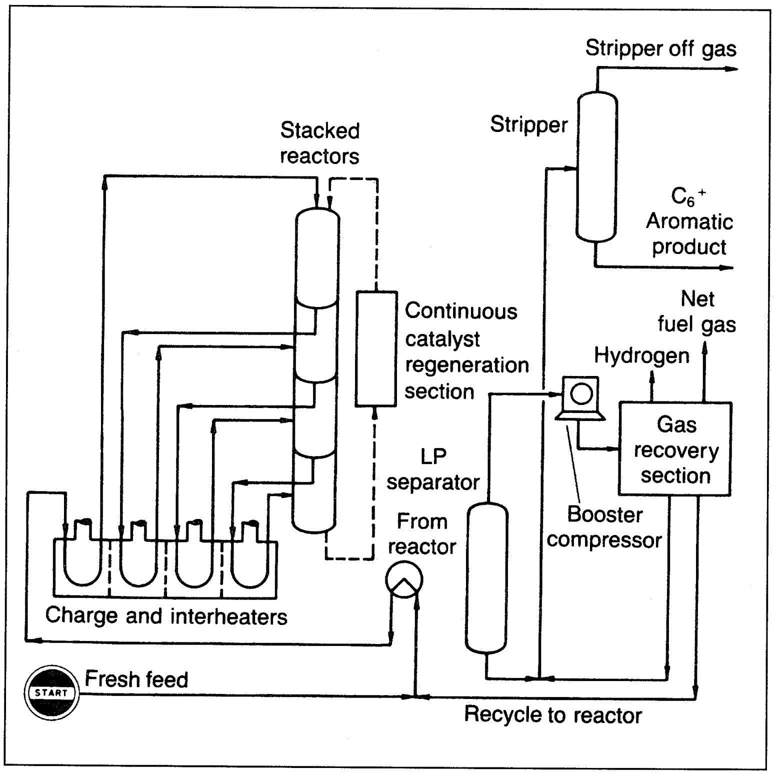


Figure 6-6. A flow diagram showing the Cyclar process for aromatization of LPG.[10]

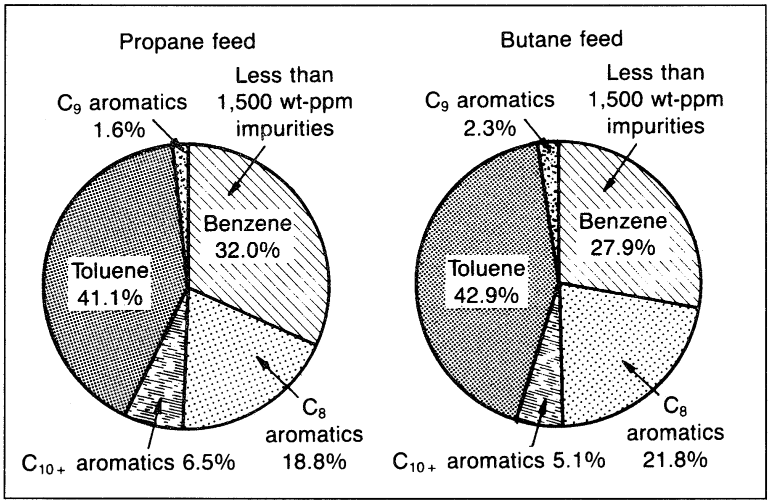


Figure 6-7. The liquid (C_6^+) product breakdown in weight units obtained from the Cyclar process.[10]

Interest in the use of lower-value light paraffins for the production of aromatics led to the introduction of two new processes similar to the Cyclar process, the Z-forming and the Aroformer processes, which were developed in Japan and Australia, respectively.[12,13]

Research is also being conducted in Japan to aromatize propane in presence of carbon dioxide using a Zn-loaded HZSM-5 catalyst.[14] The effect of CO_2 is thought to improve the equilibrium formation of aromatics by the consumption of product hydrogen (from dehydrogenation of propane) through the reverse water gas shift reaction.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

However, it was found that the effect on the equilibrium formation of aromatics is not substantial due to thermodynamic considerations. A more favorable effect was found for the reaction between ethylene (formed via cracking during aromatization of propane) and hydrogen. The reverse shift reaction consumes hydrogen and decreases the chances for the reduction of ethylene to ethane byproduct.

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3\text{-}CH_3$$

ISOMERIZATION OF n-BUTANE (Isobutane Production)

Because of the increasing demand for isobutylene for the production of oxygenates as gasoline additives, a substantial amount of n-butane is isomerized to isobutane, which is further dehydrogenated to isobutene. The Butamer process (Figure 6-8) has a fixed-bed reactor containing a highly selective catalyst that promotes the conversion of n-butane to isobutane equilibrium mixture.[15] Isobutane is then separated in a deisobutanizer tower. The n-butane is recycled with make-up hydrogen. The isomerization reaction occurs at a relatively low temperature:

$$CH_3CH_2CH_2CH_3 \rightarrow \underset{\text{Isobutane}}{CH_3CH(CH_3)_2}$$

ISOBUTANE CHEMICALS

As has been mentioned in Chapter 3, isobutane is mainly used as an alkylating agent to produce different compounds (alkylates) with a high octane number to supplement the gasoline pool. Isobutane is in high

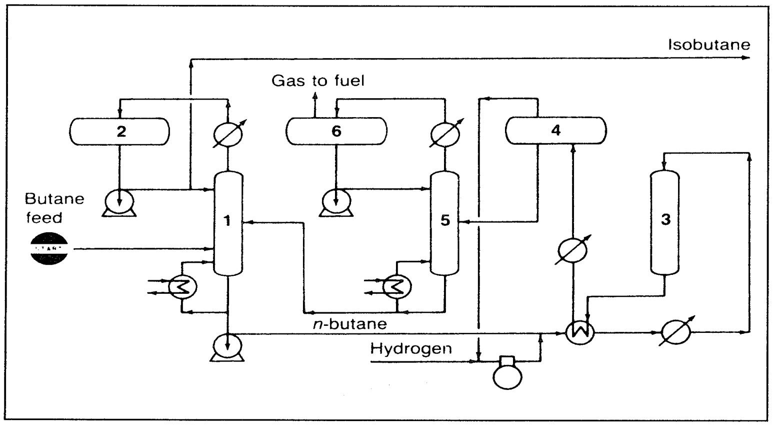


Figure 6-8. The UOP Butamer process for isomerization of n-butane to isobutane:[15] (1,2) deisobutanizer, (3) reactor, (4) separator (for separation and recycling H_2), (5,6) stabilizer.

demand as an isobutene precursor for producing oxygenates such as methyl and ethyl tertiary butyl ethers (MTBE and ETBE). The production and use of MTBE are discussed in Chapter 5. Accordingly, greater amounts of isobutane are produced from n-butane through isomerization followed by dehydrogenation to isobutene. The Catofin process is currently used to dehydrogenate isobutane to isobutene. Alternatively, isobutane could be thermally cracked to yield predominantly isobutene plus propane. Other by-products are fuel gas and C_5^+ liquid. The steam cracking process is made of three sections: a cracking furnace, a vapor recovery section, and a product fractionation section. The Coastal isobutane cracking process is reviewed by Soudek and Lacatena.[16]

NAPHTHA-BASED CHEMICALS

Light naphtha containing hydrocarbons in the C_5-C_7 range is the preferred feedstock in Europe for producing acetic acid by oxidation. Similar to the catalytic oxidation of n-butane, the oxidation of light naphtha is performed at approximately the same temperature and pressure ranges (170–200°C and ≈50 atmospheres) in the presence of manganese acetate catalyst. The yield of acetic acid is approximately 40 wt%.

$$\text{Light naphtha} + O_2 \rightarrow CH_3COOH + \text{by-products} + H_2O$$

The product mixture contains essentially oxygenated compounds (acids, alcohols, esters, aldehydes, ketones, etc.). As many as 13 distillation columns are used to separate the complex mixture. The number of products could be reduced by recycling most of them to extinction.

Manganese naphthenate may be used as an oxidation catalyst. Rouchaud and Lutete have made an in-depth study of the liquid phase oxidation of n-hexane using manganese naphthenate. A yield of 83% of C_1-C_5 acids relative to n-hexane was reported. The highest yield of these acids was for acetic acid followed by formic acid. The lowest yield was observed for pentanoic acid.[17]

In Europe naphtha is the preferred feedstock for the production of synthesis gas, which is used to synthesize methanol and ammonia (Chapter 4). Another important role for naphtha is its use as a feedstock for steam cracking units for light olefins production (Chapter 3). Heavy naphtha, on the other hand, is a major feedstock for catalytic reforming. The product reformate containing a high percentage of C_6-C_8 aromatic hydrocarbons is used to make gasoline. Reformates are also extracted to separate the aromatics as intermediates for petrochemicals.

Lecture 14

Chemicals From High Molecular Weight n-Paraffins

CHEMICALS FROM HIGH MOLECULAR WEIGHT n-PARAFFINS

High molecular weight n-paraffins are obtained from different petroleum fractions through physical separation processes. Those in the range of C_8-C_{14} are usually recovered from kerosines having a high ratio of these compounds. Vapor phase adsorption using molecular sieve 5A is used to achieve the separation. The n-paraffins are then desorbed by the action of ammonia. Continuous operation is possible by using two adsorption sieve columns, one bed on stream while the other bed is being desorbed. n-Paraffins could also be separated by forming an adduct with urea. For a paraffinic hydrocarbon to form an adduct under ambient temperature and atmospheric pressure, the compound must contain a long unbranched chain of at least six carbon atoms. Ease of adduct formation and adduct stability increases with increase of chain length.[18] Table 6-2 shows some physical properties of C_5-C_{16} n-paraffins. As with shorter-chain n-paraffins, the longer chain compounds are not highly reactive. However, they may be oxidized, chlorinated, dehydrogenated, sulfonated, and fermented under special conditions. The C_9-C_{17} paraffins are used to produce olefins or monochlorinated paraffins for the production of detergents. The 1996 capacity for the U.S., Europe, and Japan was 3.0 billion pounds.[19]

Table 6-2
Selected properties of n-paraffins from C_5-C_{16}

Name	Formula	Density	B.P.°C	M.P.°C
Pentane	$CH_3(CH_2)_3CH_3$	0.626	36.0	–130.0
Hexane	$CH_3(CH_2)_4CH_3$	0.695	69.0	–95.0
Heptane	$CH_3(CH_2)_5CH_3$	0.684	98.0	–90.5
Octane	$CH_3(CH_2)_6CH_3$	0.703	126.0	–57.0
Nonane	$CH_3(CH_2)_7CH_3$	0.718	151.0	–54.0
Decane	$CH_3(CH_2)_8CH_3$	0.730	174.0	–30.0
Undecane	$CH_3(CH_2)_9CH_3$	0.740	196.0	–26.0
Dodecane	$CH_3(CH_2)_{10}CH_3$	0.749	216.0	–10.0
Tridecane	$CH_3(CH_2)_{11}CH_3$	0.757	234.0	–6.0
Tetradecane	$CH_3(CH_2)_{12}CH_3$	0.764	252.0	5.5
Pentadecane	$CH_3(CH_2)_{13}CH_3$	0.769	266.0	10.0
Hexadecane	$CH_3(CH_2)_{14}CH_3$	0.775	280.0	18.0

OXIDATION OF PARAFFINS (Fatty Acids and Fatty Alcohols)

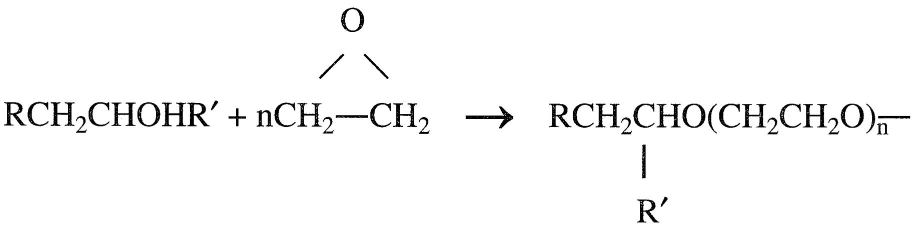
The catalytic oxidation of long-chain paraffins (C_{18}-C_{30}) over manganese salts produces a mixture of fatty acids with different chain lengths. Temperature and pressure ranges of 105–120°C and 15–60 atmospheres are used. About 60 wt% yield of fatty acids in the range of C_{12}-C_{14} is obtained. These acids are used for making soaps. The main source for fatty acids for soap manufacture, however, is the hydrolysis of fats and oils (a nonpetroleum source). Oxidation of paraffins to fatty acids may be illustrated as:

$$RCH_2(CH_2)_nCH_2CH_2R + {}^5\!/_2O_2 \rightarrow R(CH_2)_nCOOH + RCH_2COOH + H_2O$$

Oxidation of C_{12}-C_{14} n-paraffins using boron trioxide catalysts was extensively studied for the production of fatty alcohols.[20] Typical reaction conditions are 120–130°C at atmospheric pressure. ter-Butyl hydroperoxide (0.5%) was used to initiate the reaction. The yield of the alcohols was 76.2 wt% at 30.5% conversion. Fatty acids (8.9 wt%) were also obtained. Product alcohols were essentially secondary with the same number of carbons and the same structure per molecule as the parent paraffin hydrocarbon. This shows that no cracking has occurred under the conditions used. The oxidation reaction could be represented as:

$$RCH_2CH_2\,R' + {}^1\!/_2O_2 \rightarrow R\text{-}CH_2CHOHR'$$

n-Paraffins can also be oxidized to alcohols by a dilute oxygen stream (3–4%) in the presence of a mineral acid. The acid converts the alcohols to esters, which prohibit further oxidation of the alcohols to fatty acids. The obtained alcohols are also secondary. These alcohols are of commercial importance for the production of nonionic detergents (ethyoxylates):



$$RCH_2CHOHR' + n\overset{O}{\overbrace{CH_2\text{—}CH_2}} \longrightarrow RCH_2\underset{R'}{\underset{|}{C}}HO(CH_2CH_2O)_n\text{—}$$

Nonionic detergents are discussed in Chapter 7. Other uses of these alcohols are in the plasticizer field and in monoolefin production.

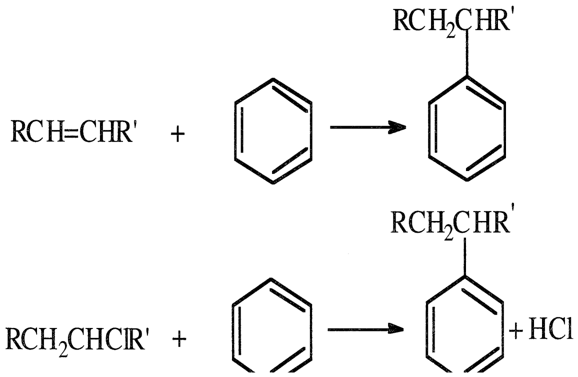
CHLORINATION OF n-PARAFFINS (Chloroparaffins)

Chlorination of n-paraffins (C_{10}-C_{14}) in the liquid phase produces a mixture of chloroparaffins. Selectivity to monochlorination could be increased by limiting the reaction to a low conversion and by decreasing the chlorine to hydrocarbon ratio. Substitution of secondary hydrogen predominates. The reaction may be represented as:

$$R\,CH_2\,CH_2R' + Cl_2 \rightarrow R\,CHCl\,CH_2R' + HCl$$

Monochloroparaffins in this range may be dehydrochlorinated to the corresponding monoolefins and used as alkylating agents for the production of biodegradable detergents. Alternatively, the monochloroparaffins are used directly to alkylate benzene in presence of a Lewis acid catalyst to produce alkylates for the detergent production. These reactions could be illustrated as follows:

$$RCH_2CHClR' \longrightarrow RCH{=}CHR' + HCl$$



Detergent production is further discussed in Chapter 10.

Polychlorination, on the other hand, can be carried out on the whole range of n-paraffins from C_{10}-C_{30} at a temperature range of 80–120°C (using a high Cl_2/paraffin ratio). The product has a chlorine content of approximately 70%. Polychloroparaffins are used as cutting oil additives, plasticizers, and retardant chemicals.

SULFONATION OF n-PARAFFINS
(Secondary Alkane Sulfonates SAS)

Linear secondary alkane sulfonates are produced by the reaction between sulfur dioxide and n-paraffins in the range of C_{15}-C_{17}.

$$R\text{-}H + 2SO_2 + 2O_2 + H_2O \rightarrow RSO_3H + H_2SO_4$$

The reaction is catalyzed by ultraviolet light with a wave-length between 3,300–3,600Å.[21] The sulfonates are nearly 100% biodegradable, soft and stable in hard water, and have good washing properties.

Sodium alkanesulfonates for detergent manufacture can also be produced from the free-radical addition of sodium bisulfite and alpha olefins:

$$RCH{=}CH_2 + NaHSO_3 \rightarrow RCH_2CH_2SO_3Na$$