

Ethylene ($\text{CH}_2=\text{CH}_2$)

- ❖ 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.

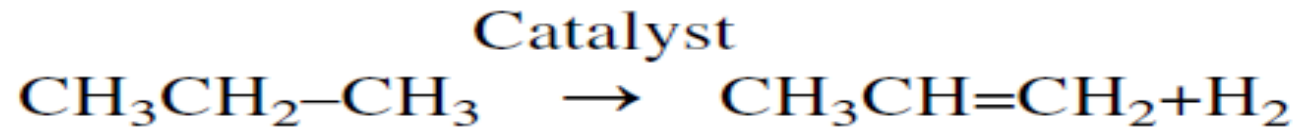
- ❖ Styrene is a monomer used in the manufacture of many commercial polymers and copolymers. Ethylene can be polymerized to different grades of polyethylenes or copolymerized with other olefins.
- ❖ Catalytic oxidation of ethylene produces ethylene oxide, which is hydrolyzed to ethylene glycol. Ethylene glycol is a monomer for the production of synthetic fibers.
- ❖ The main source for ethylene is the steam cracking of hydrocarbons.
- ❖ Table 2-2 shows the world ethylene production by source until the year 2000.4 U.S. production

Table 2-2
World ethylene production by feedstock⁴ (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 ($\text{CH}_3\text{CH}=\text{CH}_2$)

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.



- ✓ 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 (C₄H₈)

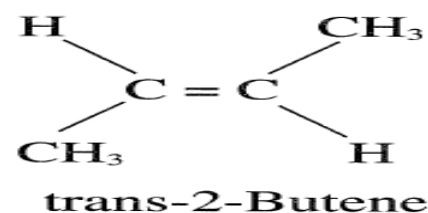
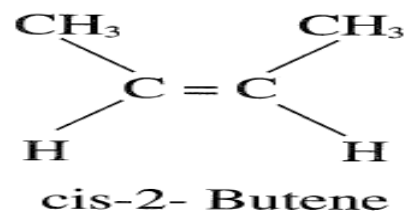
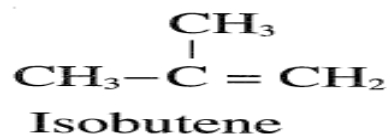
Butylenes (butenes) are by-products of refinery cracking processes and steam cracking units for ethylene production.

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:

- 1) Three unbranched,
- 2) “normal” butenes (n-butenes) and
- 3) A branched isobutene (2-methylpropene).

The three nbutenes are 1-butene and cis- and trans- 2-butene. The following shows the four butylene isomers:



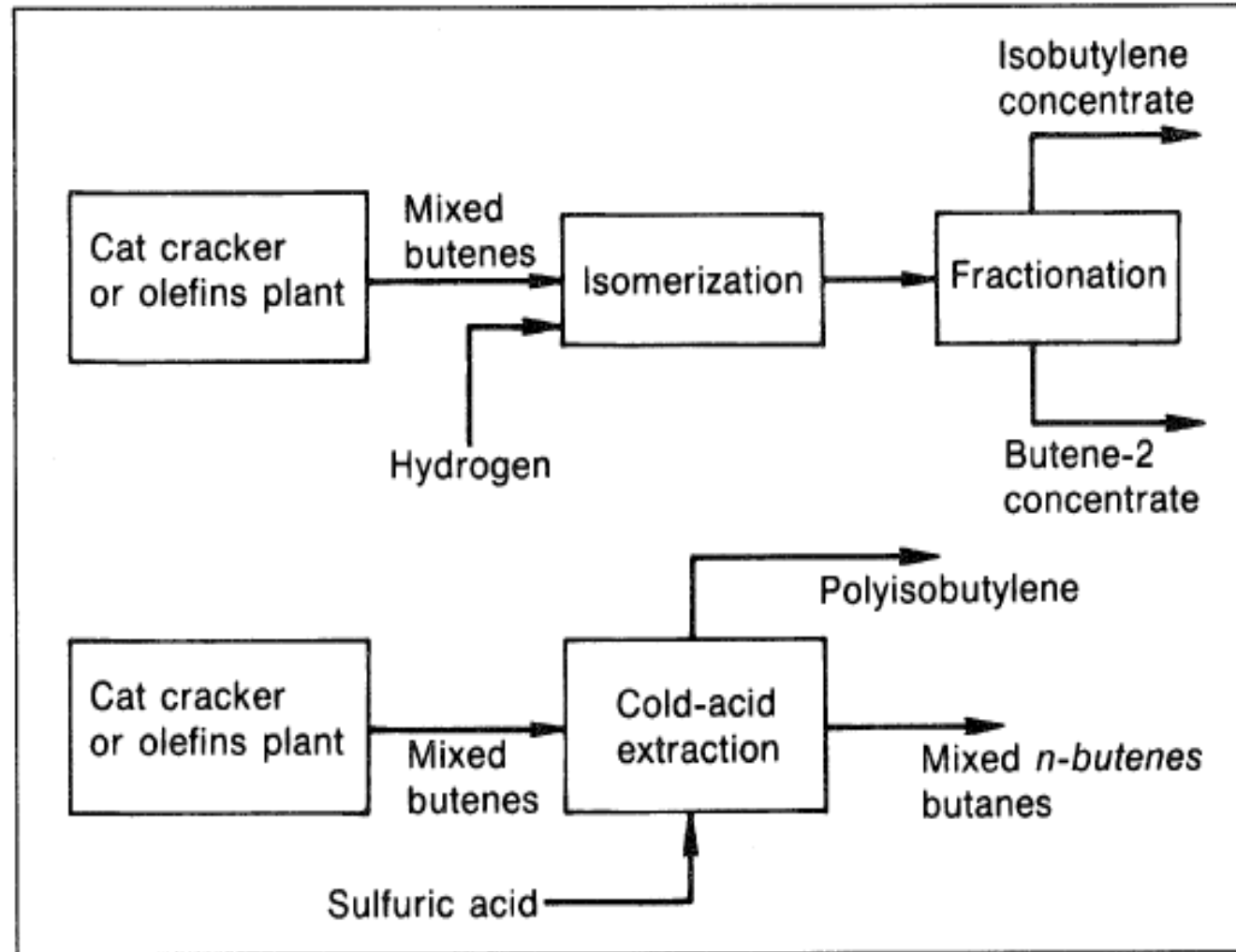


Figure 2-1. The two processes for separating n-butenes and isobutylene.⁷

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.

- ❖ 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.

Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$)

- ❖ 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.

Aromatic hydrocarbons

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- ❖ 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 reformat is rich in C6, C7, and C8 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.
- ❖ The feed (reformat), which contains a mixture of aromatics, paraffins, and naphthenes, after heat exchange with hot raffinate, is countercurrently contacted with an aqueous tetraethylene glycol solution in the extraction column.

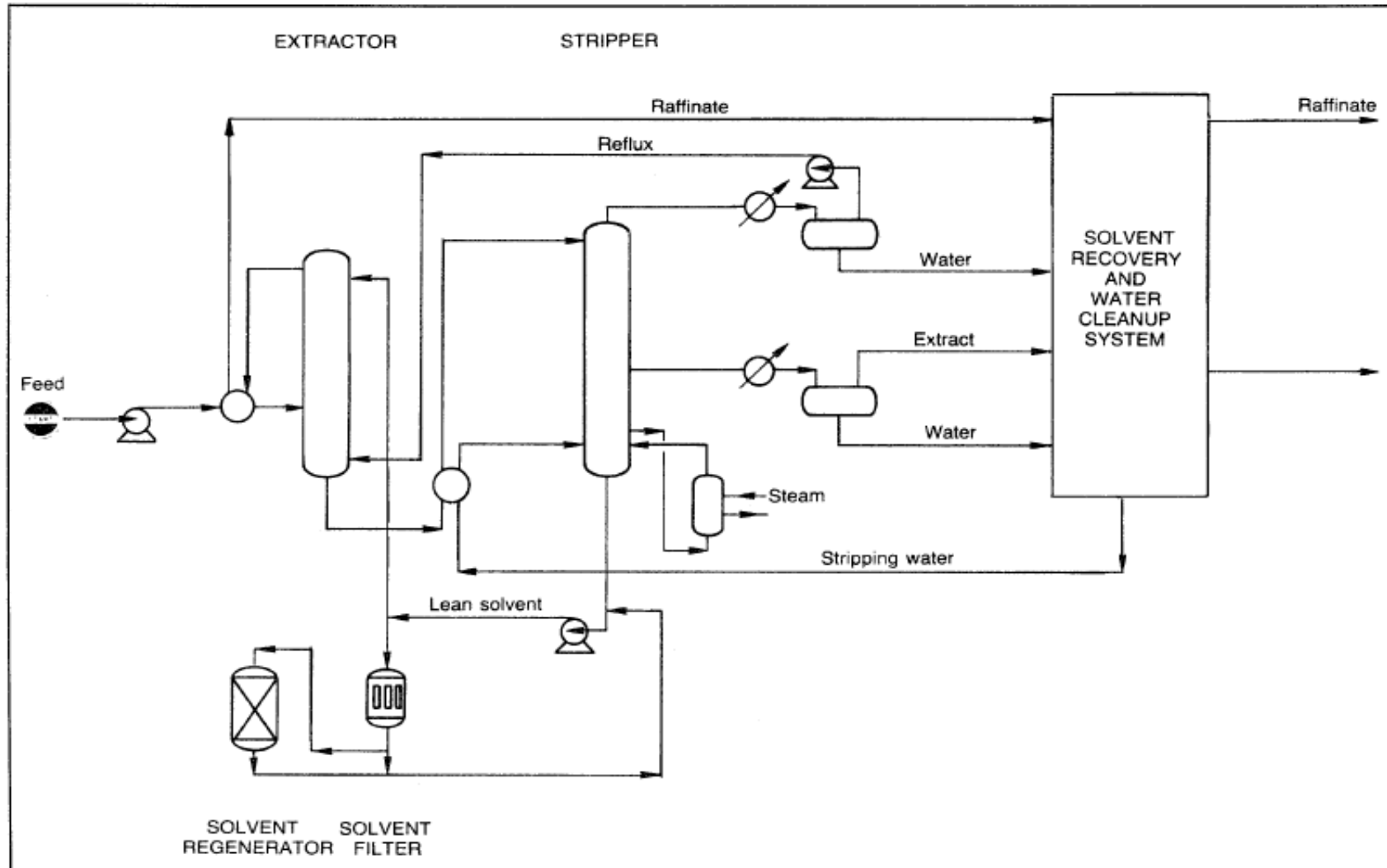
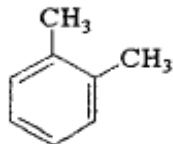
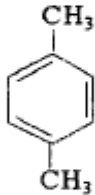
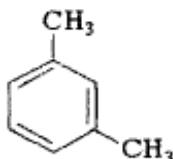
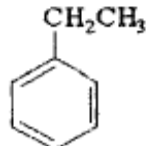


Figure 2-2. The Union Carbide aromatics extraction process using tetraethylene glycol.⁹

- ❖ 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. 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 (C8 aromatics).

- ❖ Due to the narrow range of the boiling points of C8 aromatics (Table 2-4), separation by fractional distillation is difficult. A super fractionation 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.
- ❖ The overall yield of p-xylene is increased by incorporating an isomerization unit to isomerize o- and m-xylenes to p-xylene.

Table 2-4
Boiling and freezing points of C₈ 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

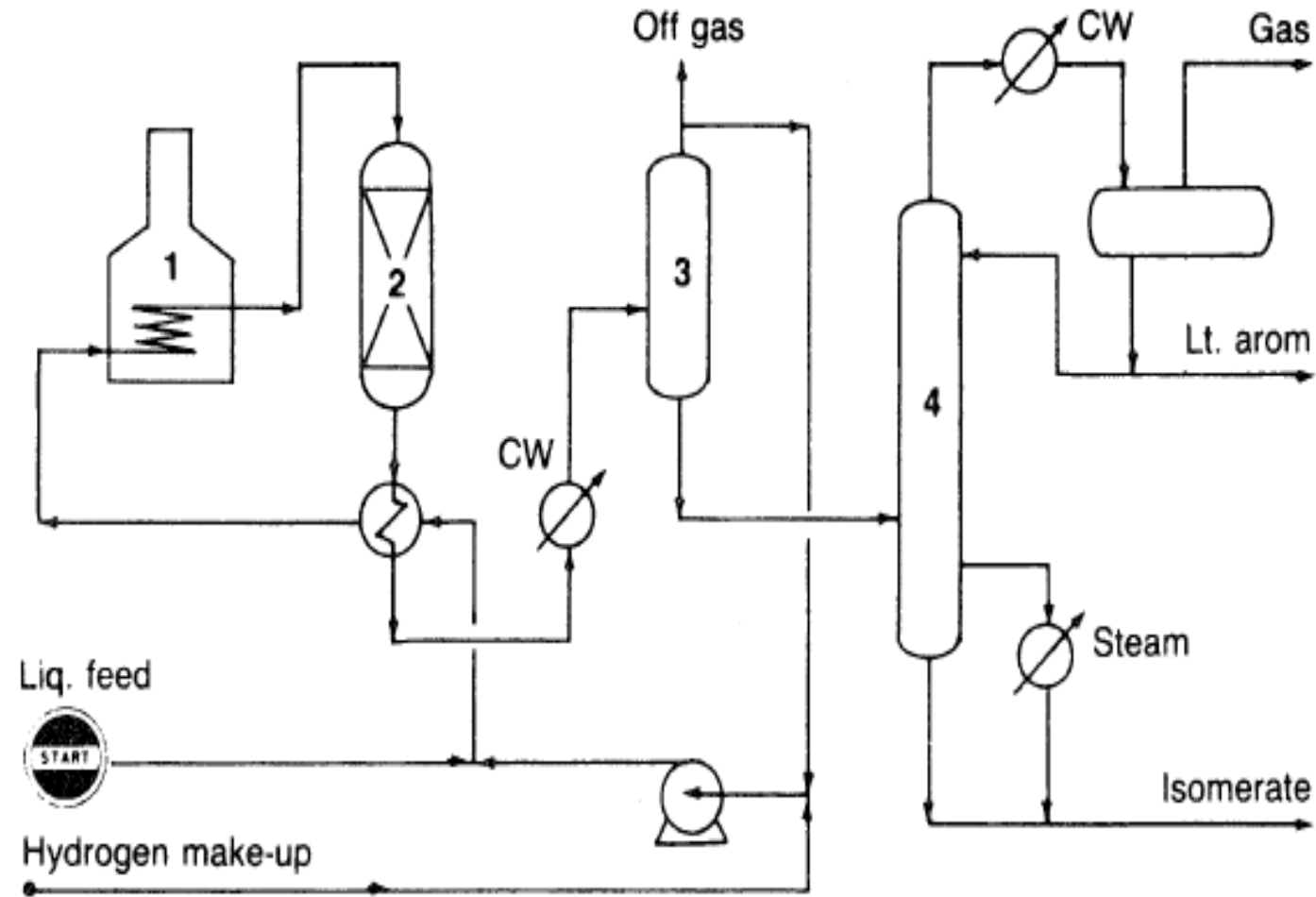
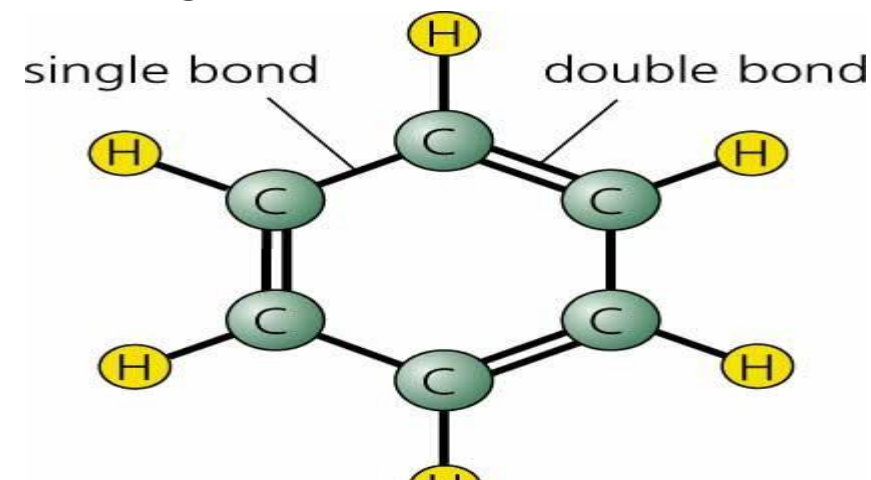


Figure 2-3. Flow diagram of the Mobil xylene isomerization process.¹²

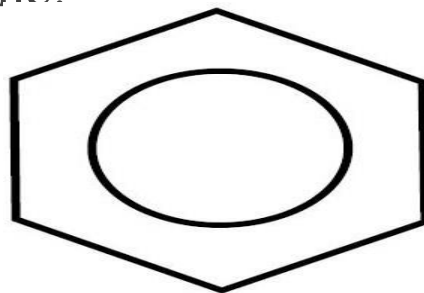
- ❖ An overall yield of 90% p-xylene could be achieved. Figure 2-3 is a flow diagram of the Mobil isomerization process. In this process, partial conversion of ethylbenzene to benzene also occurs. The catalyst used is shape selective and contains ZSM-5 zeolite.

Benzene

- ❖ Benzene (C_6H_6) is the simplest aromatic hydrocarbon and by far the most widely used one.
- ❖ Before 1940, the main source of benzene and substituted benzene was coal tar. Currently, it is mainly obtained from catalytic reforming. Other sources are pyrolysis gasolines and coal liquids.



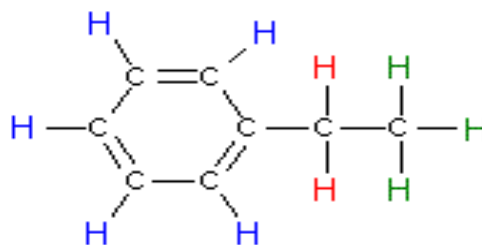
- ❖ Aromatic hydrocarbons, like paraffin hydrocarbons, react by substitution, but by a different reaction mechanism and under milder conditions.
- ❖ Aromatic compounds react by addition only under severe conditions.
- ❖ For example, electrophilic substitution of benzene using nitric acid produces nitrobenzene under normal conditions, while the addition of hydrogen to benzene occurs in presence of catalyst only under high pressure to give cyclohexane:



- ❖ Benzene is an important chemical intermediate and is the precursor for many commercial chemicals and polymers such as phenol, styrene for poly-styrenics, and caprolactom for nylon 6.

Ethylbenzene

- ❖ Ethylbenzene ($C_6H_5CH_2CH_3$) is one of the C_8 aromatic constituents in reformates and pyrolysis gasolines.
- ❖ It can be obtained by intensive fractionation of the aromatic extract, but only a small quantity of the demanded ethylbenzene is produced by this route.
- ❖ Most ethylbenzene is obtained by the alkylation of benzene with ethylene.



Ethylbenzene

Methylbenzenes (Toluene and Xylenes)

- ❖ Methylbenzenes occur in small quantities in naphtha and higher boiling fractions of petroleum.
- ❖ Those presently of commercial importance are toluene, o-xylene, p-xylene, and to a much lesser extent m-xylene.
- ❖ The primary sources of toluene and xylenes are reformates from catalytic reforming units, gasoline from catalytic cracking, and pyrolysis gasoline from steam reforming of naphtha and gas oils. As mentioned earlier, solvent extraction is used to separate these aromatics from the reformat mixture.
- ❖ Only a small amount of the total toluene and xylenes available from these sources is separated and used to produce petrochemicals.

Liquid petroleum fractions and residues

Naphtha:

- ❖ Naphtha from atmospheric distillation is characterized by an absence of olefinic compounds. Its main constituents are straight and branched chain paraffins, cycloparaffins (naphthenes), and aromatics, and the ratios of these components are mainly a function of the crude origin.
- ❖ Naphthas obtained from cracking units generally contain variable amounts of olefins, higher ratios of aromatics, and branched paraffins.
- ❖ Due to presence of unsaturated compounds, they are less stable than straight-run naphthas. On the other hand, the absence of olefins increases the stability of naphthas produced by hydrocracking units.

- ❖ In refining operations, however, it is customary to blend one type of naphtha with another to obtain a required product or feedstock.
- ❖ Selecting the naphtha type can be an important processing procedure.
- ❖ For example, a paraffinic-base naphtha is a better feedstock for steam cracking units because paraffins are cracked at relatively lower temperatures than cycloparaffins.
- ❖ Alternately, a naphtha rich in cycloparaffins would be a better feedstock to catalytic reforming units because cycloparaffins are easily dehydrogenated to aromatic compounds.

- ❖ Reformates are the main source for extracting C6-C8 aromatics used for petrochemicals. Chapter 10 discusses aromatics-based chemicals.
- ❖ Naphtha is also a major feedstock to steam cracking units for the production of olefins.
- ❖ This route to olefins is especially important in places such as Europe, where ethane is not readily available as a feedstock because most gas reservoirs produce non-associated gas with a low ethane content.
- ❖ Naphtha could also serve as a feedstock for steam reforming units for the production of synthesis gas for methanol.

PRODUCTION OF OLEFINS

- ❖ The most important olefins and diolefins used to manufacture petrochemicals are ethylene, propylene, butylenes, and butadiene. Butadiene, a conjugated diolefin, is normally coproduced with C2–C4 olefins from different cracking processes.
- ❖ Separation of these olefins from catalytic and thermal cracking gas streams could be achieved using physical and chemical separation methods.
- ❖ However, the petrochemical demand for olefins is much greater than the amounts these operations produce. Most olefins and butadienes are produced by steam cracking hydrocarbons.

STEAM CRACKING OF HYDROCARBONS

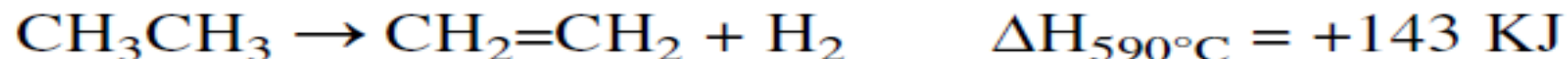
(Production of Olefins)

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The main route for producing light olefins, especially ethylene, is the steam cracking of hydrocarbons. The feedstocks for steam cracking units range from light paraffinic hydrocarbon gases to various petroleum fractions and residues. The properties of these feedstocks are discussed in Chapter 2.

The cracking reactions are principally bond breaking, and a substantial amount of energy is needed to drive the reaction toward olefin production.

The simplest paraffin (alkane) and the most widely used feedstock for producing ethylene is ethane. As mentioned earlier, ethane is obtained from natural gas liquids. Cracking ethane can be visualized as a free radical dehydrogenation reaction, where hydrogen is a coproduct:



The reaction is highly endothermic, so it is favored at higher temperatures and lower pressures. Superheated steam is used to reduce the partial pressure of the reacting hydrocarbons' (in this reaction, ethane). Superheated steam also reduces carbon deposits that are formed by the pyrolysis of hydrocarbons at high temperatures. For example, pyrolysis of ethane produces carbon and hydrogen:



Steam Cracking Process

- ❖ A typical ethane cracker has several identical pyrolysis furnaces in which fresh ethane feed and recycled ethane are cracked with steam as a diluent.
- ❖ Figure 3-12 is a block diagram for ethylene from ethane. The outlet temperature is usually in the 800°C range. The furnace effluent is quenched in a heat exchanger and further cooled by direct contact in a water quench tower where steam is condensed and recycled to the pyrolysis furnace.
- ❖ After the cracked gas is treated to remove acid gases, hydrogen and methane are separated from the pyrolysis products in the demethanizer.

- ❖ The effluent is then treated to remove acetylene, and ethylene is separated from ethane and heavier in the ethylene fractionator.
- ❖ The bottom fraction is separated in the deethanizer into ethane and C3+ fraction. Ethane is then recycled to the pyrolysis furnace.

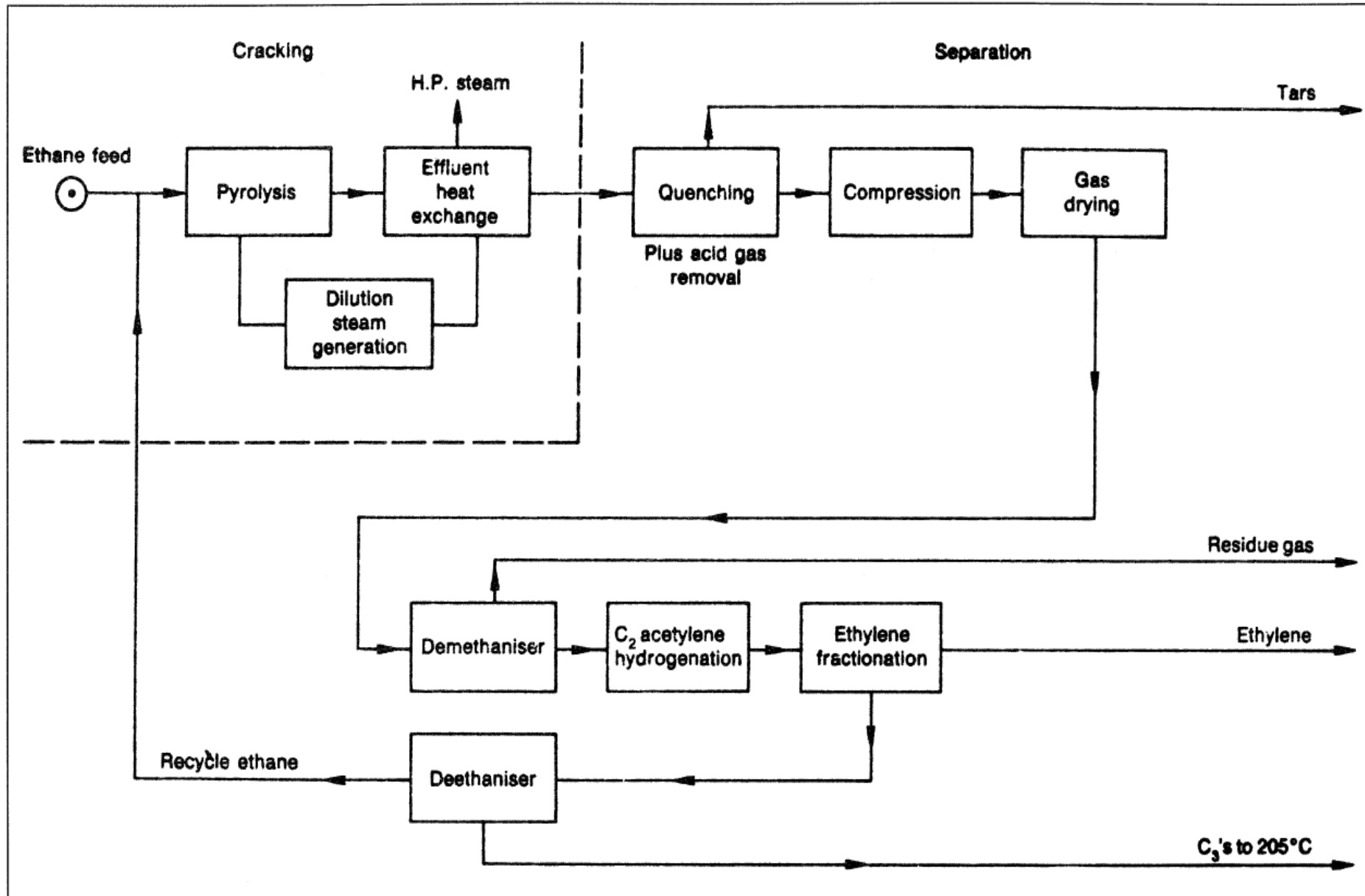


Figure 3-12. Block diagram for producing ethylene from ethane.

Process Variables:

The important process variables are reactor temperature, residence time, and steam/hydrocarbon ratio. Feed characteristics are also considered, since they influence the process severity.

1. Temperature:

Steam cracking reactions are highly endothermic. Increasing temperature favours the formation of olefins, high molecular weight olefins, and aromatics. Optimum temperatures are usually selected to maximize olefin production and minimize formation of carbon deposits.

2. Residence Time:

- ❖ In steam cracking processes, olefins are formed as primary products. Aromatics and higher hydrocarbon compounds result from secondary reactions of the formed olefins. Accordingly, short residence times are required for high olefin yield.
- ❖ When ethane and light hydrocarbon gases are used as feeds, shorter residence times are used to maximize olefin production and minimize BTX and liquid yields; residence times of
- ❖ 0.5–1.2 sec are typical.
- ❖ Cracking liquid feedstocks for the dual purpose of producing olefins plus BTX aromatics requires relatively longer residence times than for ethane.
- ❖ However, residence time is a compromise between the reaction temperature and other variables.

3. Steam/Hydrocarbon Ratio:

- ❖ A higher steam/hydrocarbon ratio favors olefin formation. Steam reduces the partial pressure of the hydrocarbon mixture and increases the yield of olefins.
- ❖ Heavier hydrocarbon feeds require more steam than gaseous feeds to additionally reduce coke deposition in the furnace tubes.
- ❖ Liquid feeds such as gas oils and petroleum residues have complex
 - ▶ polynuclear aromatic compounds, which are coke precursors.
 - ▶ Steam to hydrocarbon weight ratios range between 0.2–1 for ethane and approximately 1–1.2 for liquid feeds.

4. Feedstocks:

- ❖ Feeds to steam cracking units vary appreciably, from light hydrocarbon gases to petroleum residues. Due to the difference in the cracking rates of the various hydrocarbons, the reactor temperature and residence time vary.
- ❖ As mentioned before, long chain hydrocarbons crack more easily than shorter chain compounds and require lower cracking temperatures.
- ❖ For example, it was found that the temperature and residence time that gave 60% conversion for ethane yielded 90% conversion for propane.
- ❖ Feedstock composition also determines operation parameters. The rates of cracking hydrocarbons differ according to structure

- ❖ Paraffinic hydrocarbons are easier to crack than cycloparaffins, and aromatics tend to pass through unaffected.
- ❖ Isoparaffins such as isobutane and isopentane give high yields of propylene. This is expected, because cracking at a tertiary carbon is easier.

Cracking Liquid Feeds

- ❖ Liquid feedstocks for olefin production are light naphtha, full range naphtha, reformer raffinate, atmospheric gas oil, vacuum gas oil, residues, and crude oils. The ratio of olefins produced from steam cracking of these feeds depends mainly on the feed type and, to a lesser extent, on the operation variables.
- ❖ For example, steam cracking light naphtha produces about twice the amount of ethylene obtained from steam cracking vacuum gas oil under nearly similar conditions.
- ❖ Liquid feeds are usually cracked with lower residence times and higher steam dilution ratios than those used for gas feedstocks.

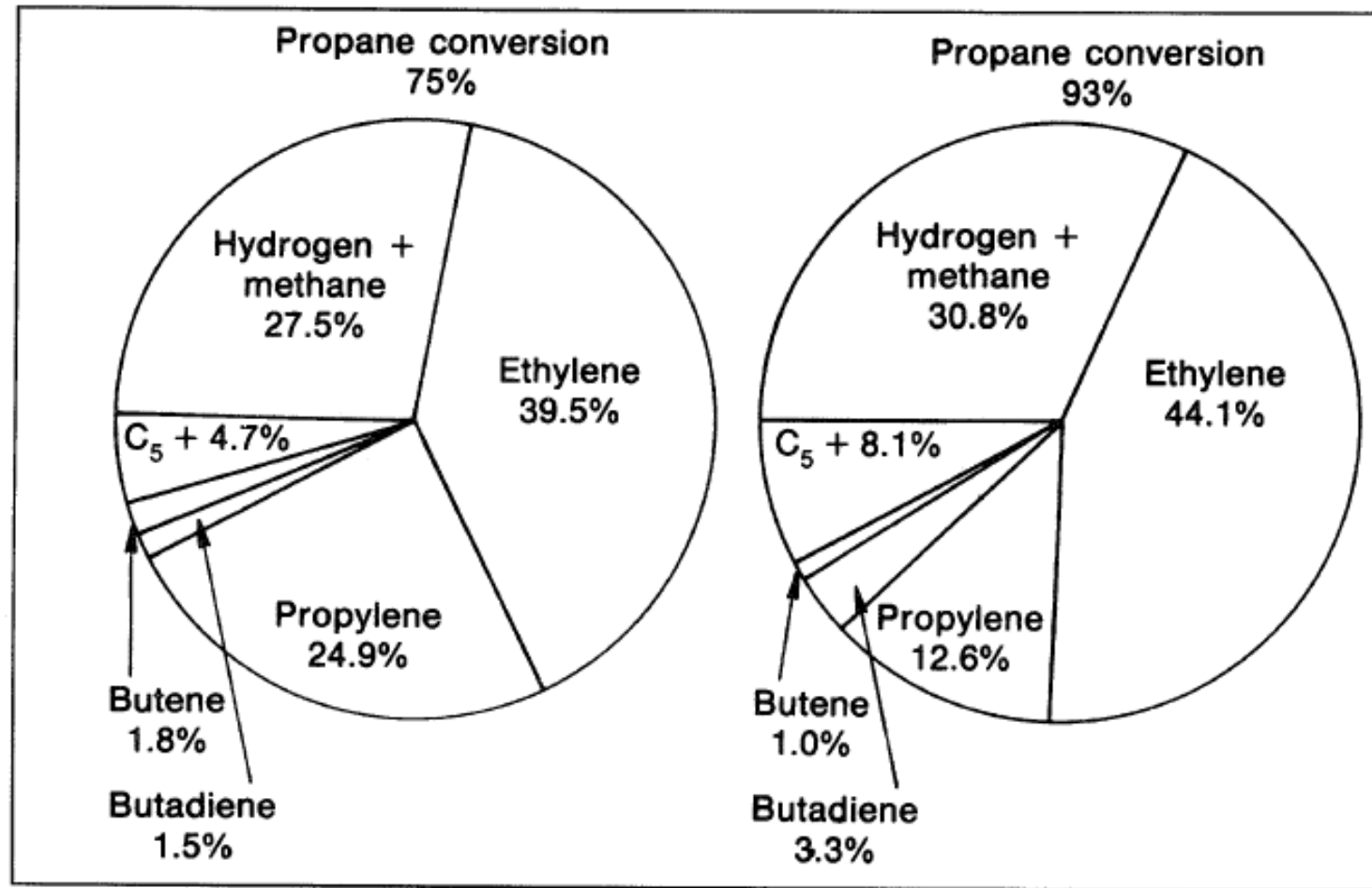


Figure 3-13. The influence of conversion severity on the theoretical product yield for the cracking of propane. Acetylene, methyl acetylene, and propadiene are hydrogenated and both ethane and propane are recycled to extinction (wt%).⁴⁶

- ❖ The reaction section of the plant is essentially the same as with gas feeds, but the design of the convection and the quenching sections are different. This is necessitated by the greater variety and quantity of coproducts.
- ❖ An additional pyrolysis furnace for cracking coproduct ethane and propane and an effluent quench exchanger are required for liquid feeds. Also, a propylene separation tower and a methyl acetylene removal unit are incorporated in the process.
- ❖ Figure 3-14 is a flow diagram for cracking naphtha or gas oil for ethylene production. As with gas feeds, maximum olefin yields are obtained at lower hydrocarbon partial pressures, pressure drops, and residence times. These variables may be adjusted to obtain higher BTX at the expense of higher olefin yield.

- ❖ One advantage of using liquid feeds over gas feedstocks for olefin production is the wider spectrum of coproducts. For example, steam cracking naphtha produces, in addition to olefins and diolefins, pyrolysis gasoline rich in BTX.
- ❖ Table 3-16 shows products from steam cracking naphtha at low and at high severities.
- ❖ It should be noted that operation at a higher severity increased ethylene product and by-product methane and decreased propylene and butenes.