

Lecture Three

CHAPTER TWO

Hydrocarbon Intermediates

INTRODUCTION

Natural gas and crude oils are the main sources for hydrocarbon intermediates or secondary raw materials for the production of petrochemicals. From natural gas, ethane and LPG are recovered for use as intermediates in the production of olefins and diolefins. Important chemicals such as methanol and ammonia are also based on methane via synthesis gas. On the other hand, refinery gases from different crude oil processing schemes are important sources for olefins and LPG. Crude oil distillates and residues are precursors for olefins and aromatics via cracking and reforming processes.

PARAFFINIC HYDROCARBONS

Paraffinic hydrocarbons used for producing petrochemicals range from the simplest hydrocarbon, methane, to heavier hydrocarbon gases and liquid mixtures present in crude oil fractions and residues.

Paraffins are relatively inactive compared to olefins, diolefins, and aromatics. Few chemicals could be obtained from the direct reaction of paraffins with other reagents. However, these compounds are the precursors for olefins through cracking processes. The C_6 – C_9 paraffins and cycloparaffins are especially important for the production of aromatics through reforming.

METHANE (CH₄)

Methane is the first member of the alkane series and is the main component of natural gas. It is also a by-product in all gas streams from processing crude oils. It is a colorless, odorless gas that is lighter than air.

As a chemical compound, methane is not very reactive. It does not react with acids or bases under normal conditions. It reacts, however, with a limited number of reagents such as oxygen and chlorine under specific conditions. For example, it is partially oxidized with a limited amount of oxygen to a carbon monoxide-hydrogen mixture at high temperatures in presence of a catalyst. The mixture (synthesis gas) is an important building block for many chemicals. Methane is mainly used as a clean fuel gas. Approximately one million BTU are obtained by burning 1,000 ft³ of dry natural gas (methane). It is also an important source for carbon black.

Methane may be liquefied under very high pressures and low temperatures. Liquefaction of natural gas (methane), allows its transportation to long distances through cryogenic tankers.

ETHANE (CH₃-CH₃)

Ethane is an important paraffinic hydrocarbon intermediate for the production of olefins, especially ethylene. It is the second member of the alkanes and is mainly recovered from natural gas liquids.

Ethane, like methane, is a colorless gas that is insoluble in water. It does not react with acids and bases, and is not very reactive toward many reagents. It can also be partially oxidized to a carbon monoxide and hydrogen mixture or chlorinated under conditions similar to those used for methane. When ethane is combusted in excess air, it produces carbon dioxide and water with a heating value of 1,800 Btu/ft³ (approximately double that produced from methane).

As a constituent of natural gas, ethane is normally burned with methane as a fuel gas. Ethane's relation with petrochemicals is mainly through its cracking to ethylene. Ethylene is the largest end use of ethane in the U.S. while it is only 5% in Western Europe.

PROPANE (CH₃CH₂CH₃)

Propane is a more reactive paraffin than ethane and methane. This is due to the presence of two secondary hydrogens that could be easily substituted. Propane is obtained from natural gas liquids or from refinery gas streams. Liquefied petroleum gas (LPG) is a mixture of propane and butane and is mainly used as a fuel. The heating value of propane is 2,300 Btu/ft³. LPG is currently an important feedstock for the production of olefins for petrochemical use.

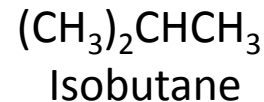
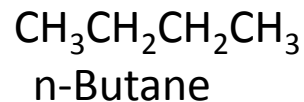
Liquid propane is a selective hydrocarbon solvent used to separate paraffinic constituents in lube oil base stocks from harmful asphaltic materials. It is also a refrigerant for liquefying natural gas and used for the recovery of condensable hydrocarbons from natural gas.

Chemicals directly based on propane are few, although as mentioned, propane and LPG are important feedstocks for the production of olefins.

BUTANES (C₄H₁₀)

Like propane, butanes are obtained from natural gas liquids and from refinery gas streams. The C₄ acyclic paraffin consists of two isomers: n-butane and isobutane (2-methylpropane). The physical as well as the chemical properties of the two isomers are quite different due to structural differences. For example, the vapor pressure (Reid method) for n-butane is 52 lb/in.², while it is 71 lb/in.² for isobutane. This makes the former a more favorable gasoline additive to adjust its vapor pressure. However, this use is declining in the United States due to new regulations that reduce the volatility of gasolines to 9 psi, primarily by removing butane.

Isobutane, on the other hand, is a much more reactive compound due to the presence of a tertiary hydrogen.



Butane is primarily used as a fuel gas within the LPG mixture. Like ethane and propane, the main chemical use of butane is as feedstock for steam cracking units for olefin production. Dehydrogenation of n-butane to butenes and to butadiene is an important route for the production of synthetic rubber. n-Butane is also a starting material for acetic acid and maleic anhydride production .

Due to its higher reactivity, isobutane is an alkylating agent of light olefins for the production of alkylates. Alkylates are a mixture of branched hydrocarbons in the gasoline range having high octane ratings. Dehydrogenation of isobutane produces isobutene, which is a reactant for the synthesis of methyl tertiary butyl ether (MTBE). This compound is currently in high demand for preparing unleaded gasoline due to its high octane rating and clean burning properties.

OLEFINIC HYDROCARBONS

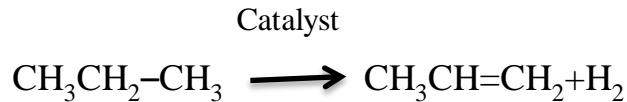
The most important olefins used for the production of petrochemicals are ethylene, propylene, the butylenes, and isoprene. These olefins are usually coproduced with ethylene by steam cracking of ethane, LPG, liquid petroleum fractions, and residues. Olefins are characterized by their higher reactivities 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 (CH₂=CH₂)

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. 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. U.S. production of ethylene was approximately 51 billion lbs in 1997.

PROPYLENE (CH₃CH=CH₂)

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.



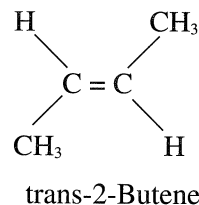
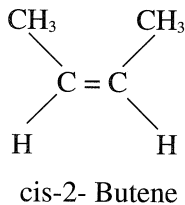
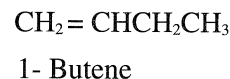
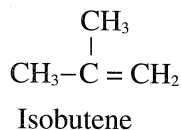
Propylene can be polymerized alone or copolymerized with other monomers such as ethylene. Many important chemicals are based on propylene such as isopropanol, allyl alcohol, glycerol, and acrylonitrile.

BUTYLENES (C₄H₈)

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

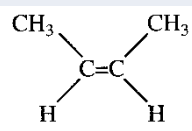
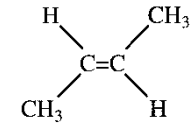
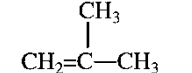
Dehydrogenation of butanes is a second source of butenes. However, this source is becoming more important because isobutylene (a butene isomer) is currently highly demanded for the production of oxygenates as gasoline additives.

There are four butene isomers: 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:



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 2-36 shows the boiling points of the different butene isomers.

Table 2-3
Structure and boiling points of C4 olefins

Name	Structure	Boiling Point°C
1-Butene	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	-6.3
Cis-2-Butene		+3.7
trans-2-Butene		+0.9
Isobutene		-6.6

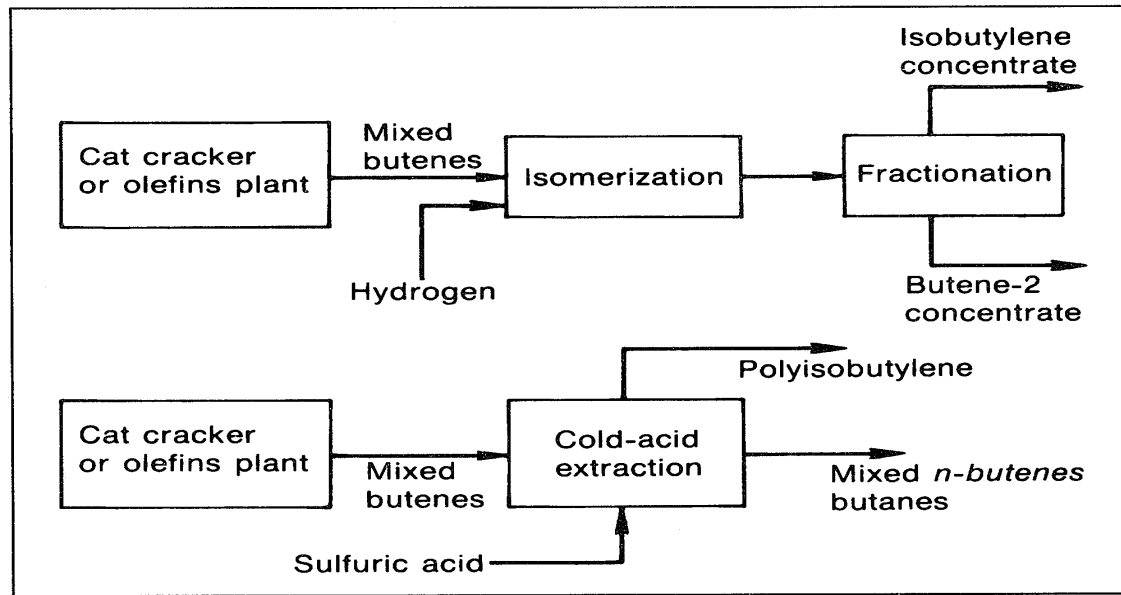


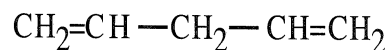
Figure 2-1. The two processes for separating n-butenes and isobutylene.

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.

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.

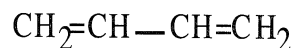
Examples of nonconjugated dienes are 1,4-pentadiene and 1,4-cyclohexadiene. Examples of conjugated dienes are 1,3-butadiene and 1,3-cyclohexadiene.



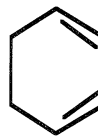
1,4-Pentadiene



1,4-Cyclohexadiene



1,3-Butadiene



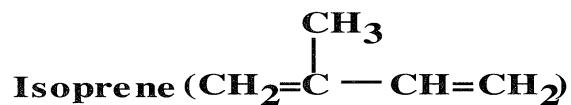
1,3-Cyclohexadiene

BUTADIENE (CH₂=CH-CH=CH₂)

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.



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 C₅ olefins (tertiary amylenes) obtained by the extraction of a C₅ fraction from catalytic cracking units. It can also be produced through several synthetic routes using reactive chemicals such as isobutene, formaldehyde, and propene. 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 reformat is rich in C₆, C₇, and C₈ aromatics, which could be extracted by a suitable solvent such as sulfolane or ethylene glycol.

The extract, which is composed of BTX and ethylbenzene, is then fractionated. Benzene and toluene are recovered separately, and ethyl-benzene 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. An overall yield of 90% p-xylene could be achieved.