

# CHAPTER 2

## Hydrocarbon Intermediates

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## 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.

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## 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 C6-C9 paraffins and cycloparaffins are especially important for the production of aromatics through reforming.

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# PARAFFINIC HYDROCARBONS

Table 2-1  
Selected physical properties of C<sub>1</sub>-C<sub>4</sub> paraffins

Name	Formula	Specific gravity	Boiling point °C	Calorific value Btu/ft <sup>3</sup>
Methane	CH <sub>4</sub>	0.554*	-161.5	1,009
Ethane	CH <sub>3</sub> CH <sub>3</sub>	1.049*	-88.6	1,800
Propane	CH <sub>3</sub> CH <sub>2</sub> H <sub>3</sub>	1.562*	-42.1	2,300
n-Butane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	0.579	-0.5	3,262
Isobutane	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>3</sub>	0.557	-11.1	3,253

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# METHANE

- 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.
- Table 2-1 shows selected physical properties of C<sub>1</sub>-C<sub>4</sub> paraffinic hydrocarbon gases.
- 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.

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# METHANE

- Methane is mainly used as a clean fuel gas. Approximately one million BTU are obtained by burning 1,000 ft<sup>3</sup> 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.

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## ETHANE

- 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/ft<sup>3</sup> (approximately double that produced from methane).

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## PROPANE

- 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/ft<sup>3</sup>.
- LPG is currently an important feedstock for the production of olefins for petrochemical use.

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## PROPANE

- 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.

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## BUTANES

- Like propane, butanes are obtained from natural gas liquids and from refinery gas streams. The C<sub>4</sub> 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.<sup>2</sup>, while it is 71 lb/in.<sup>2</sup> 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.

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## BUTANES

- Isobutane is a much more reactive compound due to the presence of a tertiary hydrogen.  
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \quad (\text{CH}_3)_2\text{CHCH}_3$$

**n-Butane**                      **Isobutane**
- 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.

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## BUTANES

- 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 in high demand for preparing unleaded gasoline due to its high octane rating and clean burning properties.

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## 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.

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## ETHYLENE (CH<sub>2</sub>=CH<sub>2</sub>)

- 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 to 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.

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## ETHYLENE (CH<sub>2</sub>=CH<sub>2</sub>)

- 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

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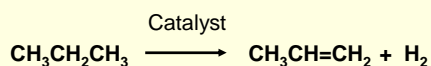
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## PROPYLENE (CH<sub>3</sub>CH=CH<sub>2</sub>)

- 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.

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## BUTYLENES (C<sub>4</sub>H<sub>8</sub>)

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

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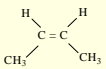
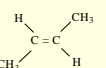

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## BUTYLENES (C<sub>4</sub>H<sub>8</sub>)

### Structure and boiling points of C<sub>4</sub> olefins

Name	Structure	Boiling Point, °C
1-Butene	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>3</sub>	-6.3
<i>cis</i> -2-Butene		+3.7
<i>trans</i> -2-Butene		+0.9
Isobutene		-6.6

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## BUTYLENES (C<sub>4</sub>H<sub>8</sub>)

- 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%.
- An alternative method for separating the butanes 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

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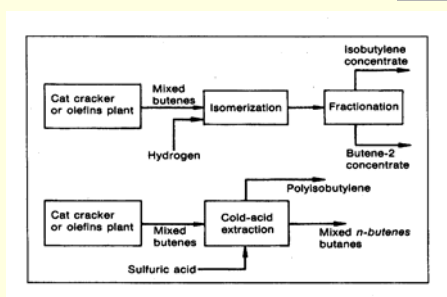
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## BUTYLENES (C<sub>4</sub>H<sub>8</sub>)



The two processes for separating n-butenes and isobutylene

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## 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-cyclo-hexadiene. Examples of conjugated dienes are 1,3-butadiene and 1,3-cyclohexadiene.

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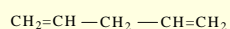
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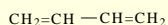
## DIENES



1,4-Pentadiene



1,4-Cyclohexadiene



1,3-Butadiene

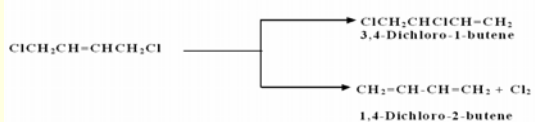


1,3-Cyclohexadiene

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## DIENES

- 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:



When polymerizing dienes for synthetic rubber production, coordination catalysts are used to direct the reaction to yield predominantly 1,4-addition polymers

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## 1,3-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.

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## 1,3-BUTADIENE ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ )

- Butadiene is obtained mainly as a co-product 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.

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## ISOPRENE [ $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$ ]

- Isoprene (2-methyl-1,3-butadiene) is a colorless liquid, soluble in alcohol but not in water. Its boiling temperature is  $34.1^\circ\text{C}$ .
- 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.

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## 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  $\pi$ -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.

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## 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 C6, C7, and C8 aromatics, which could be extracted by a suitable solvent such as sulfolane or tetraethylene 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 uses tetraethylene glycol as a solvent.
- The feed (reformate), 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.

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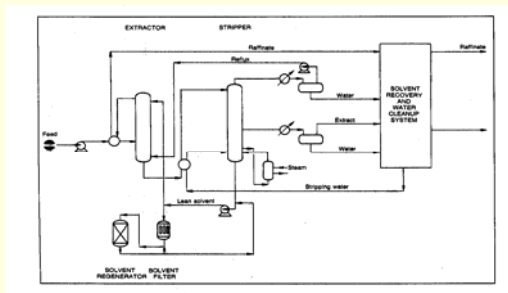
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## EXTRACTION OF AROMATICS



The Union Carbide aromatics extraction process using tetraethylene glycol

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## EXTRACTION OF AROMATICS

- 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.
- 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 (C9 aromatics).

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## EXTRACTION OF AROMATICS

- Due to the narrow range of the boiling points of C8 aromatics, 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. The overall yield of *p*-xylene is increased.

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



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## EXTRACTION OF AROMATICS

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

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## EXTRACTION OF AROMATICS

- 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.

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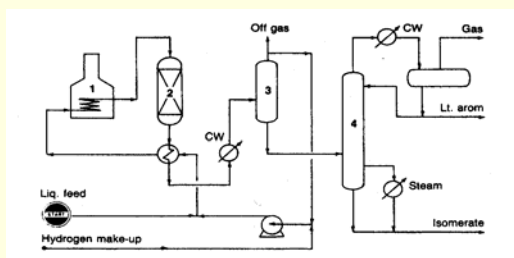
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## EXTRACTION OF AROMATICS



Flow diagram of the Mobil xylene isomerization process

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## BENZENE

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

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## ETHYLBENZENE

- Ethylbenzene ( $C_6H_5CH_2CH_3$ ) is one of the C8 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. Chapter 10 discusses conditions for producing ethylbenzene with benzene chemicals.
- Essentially, ethylbenzene is used for the production of styrene.

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## METHYLBENZENES

- 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 catcracking, and pyrolysis gasoline from steam reforming of naphtha and gas oils.
- Solvent extraction is used to separate these aromatics from the reformate mixture.
- Only a small amount of the total toluene and xylenes available from these sources is separated and used to produce petrochemicals.

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## METHYLBENZENES

- Toluene and xylenes have chemical characteristics similar to benzene, but these characteristics are modified by the presence of the methyl substituents.
- Although such modification activates the ring, toluene and xylenes have less chemicals produced from them than from benzene.
- Currently, the largest single use of toluene is to convert it to benzene.
- Para-Xylene is mainly used to produce terephthalic acid for polyesters. o-Xylene is mainly used to produce phthalic anhydride for plasticizers.

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TABLE 2.2 Crude Oil Distillation

Fraction	Boiling Point Range	Comments
<b>1. Gases</b> Methane (65–90%) ethane, propane, butane	Below 20°C	Similar to natural gas. Useful for fuel and chemicals. Also obtained from catalytic cracking and catalytic reforming. Much of it flared because of cost of recovery. n-Butane, however, is practically always recovered.
<b>2. Naphtha</b> Light naphtha (C <sub>5</sub> , C <sub>6</sub> hydrocarbons)	70–140°C	Naphtha is predominantly C <sub>5</sub> –C <sub>9</sub> aliphatic and cycloaliphatic compounds. May contain some aromatics. Base for gasoline. Useful for both fuel and chemicals. Light naphtha now considered undesirable in gasoline because catalytic reforming yields benzene, which is toxic and has a relatively low-octane number.
Heavy naphtha (C <sub>7</sub> –C <sub>9</sub> hydrocarbons)	140–200°C	
<b>3. Atmospheric gas oil</b> Kerosene	175–275°C	Contains C <sub>9</sub> –C <sub>16</sub> compounds useful for jet, tractor, and heating fuel.
Diesel fuel	200–370°C	Contains C <sub>13</sub> –C <sub>25</sub> compounds, mostly linear. Useful for diesel and heating fuels. Gas oil is catalytically cracked to naphtha and may be steam cracked to olefins.
<b>4. Heavy fractions</b> Lubricating oil Residual or heavy fuel oil	Above 370°C	Used for lubrication Used for boiler fuel. Vacuum distillation gives vacuum gas oil for catalytic cracking.
Asphalt or "resid"		Used for paving, coating and structural applications.

## LIQUID PETROLEUM FRACTIONS AND RESIDUES

- Liquid Petroleum fractions are light naphtha, heavy naphtha, kerosine and gas oil.
- The bottom product from distillation units is the residue. These mixtures are intermediates through which other reactive intermediates are obtained.
- Heavy naphtha is a source of aromatics via catalytic reforming and of olefins from steam cracking units.
- Gas oils and residues are sources of olefins through cracking and pyrolysis processes.

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## Naphtha

- Naphtha is a generic term normally used in the petroleum refining industry for the overhead liquid fraction obtained from atmospheric distillation units.
- The approximate boiling range of light straight-run naphtha (LSR) is 35-90°C, while it is about 80-200°C for heavy straight-run naphtha (HSR).
- Naphtha is also obtained from other refinery processing units such as catalytic cracking, hydrocracking, and coking units.
- The composition of naphtha, which varies appreciably, depends mainly on the crude type and whether it is obtained from atmospheric distillation or other processing units.

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## 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.

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## Naphtha

- 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.
- The main use of naphtha in the petroleum industry is in gasoline production.
- Light naphtha is normally blended with reformed gasoline (from catalytic reforming units) to increase its volatility and to reduce the aromatic content of the product gasoline.

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## Naphtha

- Heavy naphtha from atmospheric distillation units or hydrocracking units has a low octane rating, and it is used as a feedstock to catalytic reforming units.
- Catalytic reforming is a process of upgrading low octane naphtha to a high-octane reformat by enriching it with aromatics and branched paraffins. The octane rating of gasoline fuels is a property related to the spontaneous ignition of unburned gases before the flame front and causes a high pressure.
- A fuel with a low octane rating produces a strong knock, while a fuel with a high octane rating burns smoothly without detonation.
- Octane rating is measured by an arbitrary scale in which isooctane (2,2,4-trimethylpentane) is given a value of 100 and n-heptane a value of zero. A fuel's octane number equals the percentage of isooctane in a blend with n-heptane.

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## Naphtha

**Table 2-5**  
Typical analyses of two straight-run naphtha fractions from two crude types

Test	Marine Balayem Egypt	Bakr-9 Egypt
Boiling range °C	58-170	71-182
Specific gravity 60/160°F	0.7485	0.7350
°API	57.55	
Sulfur content wt %	0.055	0.26
Hydrocarbon types vol %		
Paraffins	62.7	80.2
Naphthenes	29.1	11.0
Aromatics	8.2	8.8

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## Naphtha

Table 2-6  
Boiling points and octane ratings of different hydrocarbons in the gasoline range

Hydrocarbon	Boiling point, °F	Octane number clear	
		Research method F-1	Motor method F-2
n-Butane	0.5	...	...
n-Pentane	97	61.7	61.9
2-Methylbutane	82	92.3	90.3
2,2-Dimethylbutane	122	91.8	93.4
2,3-Dimethylbutane	137	103.5	94.3
n-Hexane	156	24.8	26.0
2-Methylpentane	146	73.4	73.5
3-Methylpentane	140	74.5	74.3
n-Heptane	208	0.0	0.0
2-Methylhexane	194	42.4	46.4
n-Octane	258	-19.0*	-15.0*
2,2,4-Trimethyl pentane (isooctane)	211	100.0	100.0
Benzene	176	...	114.8
Toluene	231	120.1	103.5
Ethylbenzene	278	107.4	97.9
Isopropylbenzene	306	...	...
o-Xylene	292	120.0*	103.0*
m-Xylene	283	145.0	124.0*
p-Xylene	281	146.0*	127.0*

\* Blending value of 20% in 60 octane number reference fuel.

## Naphtha

- The octane number is measured using a single-cylinder engine (CFR engine) with a variable compression ratio.
- The octane number of a fuel is a function of the different hydrocarbon constituents present.
- In general, aromatics and branched paraffins have higher octane ratings than straight-chain paraffins and cycloparaffins.
- 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.

## KEROSINE

- Kerosine, a distillate fraction heavier than naphtha, is normally a product from distilling crude oils under atmospheric pressures. It may also be obtained as a product from thermal and catalytic cracking or hydrocracking units.
- Kerosines from cracking units are usually less stable than those produced from atmospheric distillation and hydrocracking units due to presence of variable amounts of olefinic constituents.
- Kerosine is usually a clear colorless liquid which does not stop flowing except at very low temperature (normally below -30°C).
- However, kerosine containing high olefin and nitrogen contents may develop some color (pale yellow) after being produced.

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## KEROSINE

- The main constituents of kerosine obtained from atmospheric and hydrocracking units are paraffins, cycloparaffins, and aromatics.
- Kerosines with a high normal-paraffin content are suitable feedstocks for extracting C12-C14 n-paraffins, which are used for producing biodegradable detergents.
- Currently, kerosine is mainly used to produce jet fuels, after it is treated to adjust its burning quality and freezing point.
- Before the widespread use of electricity, kerosine was extensively used to fuel lamps, and is still used for this purpose in remote areas. It is also used as a fuel for heating purposes.

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## GAS OIL

- Gas oil is a heavier petroleum fraction than kerosene. It can be obtained from the atmospheric distillation of crude oils (atmospheric gas oil, AGO), from vacuum distillation of topped crudes (vacuum gas oil, VGO), or from cracking and hydrocracking units.
- Atmospheric gas oil has a relatively lower density and sulfur content than vacuum gas oil produced from the same crude.
- The aromatic content of gas oils varies appreciably, depending mainly on the crude type and the process to which it has been subjected.
- For example, the aromatic content is approximately 10% for light gas oil and may reach up to 50% for vacuum and cracked gas oil.

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## GAS OIL

- A major use of gas oil is as a fuel for diesel engines.
- Another important use is as a feedstock to cracking and hydrocracking units.
- Gases produced from these units are suitable sources for light olefins and LPG.
- Liquefied petroleum gas LPG may be used as a fuel, as a feedstock to steam cracking units for olefin production, or as a feedstock for a Cyclar unit for the production of aromatics.

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## GAS OIL

Table 2-7  
Characteristics of typical atmospheric gas oil (AGO) and  
vacuum gas oil (VGO)

Properties	Gas oil	
	Atmospheric AGO	Vacuum VGO
Specific gravity, °API	38.6	30.0
Specific gravity, 15/15°C	0.832	0.876
Boiling range, °C	232-327	299-538
Hydrogen, wt %	13.7	13.0
Aromatics, wt %	24.0	28.0

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## RESIDUAL FUEL OIL

- Residual fuel oil is generally known as the bottom product from atmospheric distillation units. Fuel oils produced from cracking units are unstable. When used as fuels, they produce smoke and deposits that may block the burner orifices.
- The constituents of residual fuels are more complex than those of gas oils. A major part of the polynuclear aromatic compounds, asphaltenes, and heavy metals found in crude oils is concentrated in the residue.
- The main use of residual fuel oil is for power generation. It is burned in direct-fired furnaces and as a process fuel in many petroleum and chemical companies. Due to the low market value of fuel oil, it is used as a feedstock to catalytic and thermal cracking units.

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## RESIDUAL FUEL OIL

- Residues containing high levels of heavy metals are not suitable for catalytic cracking units.
- These feedstocks may be subjected to a demetallization process to reduce their metal contents.
- For example, the metal content of vacuum residues could be substantially reduced by using a selective organic solvent such as pentane or hexane, which separates the residue into an oil (with a low metal and asphaltene content) and asphalt (with high metal content).
- Demetallized oils could be processed by direct hydrocatalysis.

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## RESIDUAL FUEL OIL

- Another approach used to reduce the harmful effects of heavy metals in petroleum residues is metal passivation.
- In this process an oil-soluble treating agent containing antimony is used that deposits on the catalyst surface in competition with contaminant metals, thus reducing the catalytic activity of these metals in promoting coke and gas formation.
- Metal passivation is especially important in fluid catalytic cracking (FCC) processes. Additives that improve FCC processes were found to increase catalyst life and improve the yield and quality of products.

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## RESIDUAL FUEL OIL

- Residual fuels with high heavy metal content can serve as feedstocks for thermal cracking units such as delayed coking.
- Low-metal fuel oils are suitable feedstocks to catalytic cracking units. Product gases from cracking units may be used as a source for light olefins and LPG for petrochemical production.
- Residual fuel oils are also feedstocks for steam cracking units for the production of olefins.

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