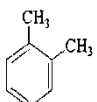
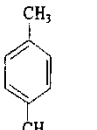
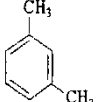
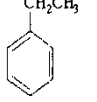


Lecture Four

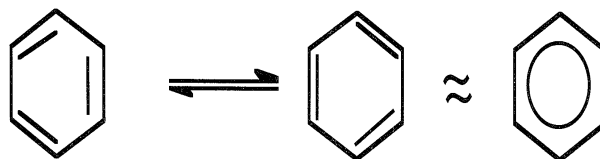
Table 2-4
Boiling and freezing points of C₈ aromatics

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

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.

Benzene has a unique structure due to the presence of six delocalized π electrons that encompass the six carbon atoms of the hexagonal ring.



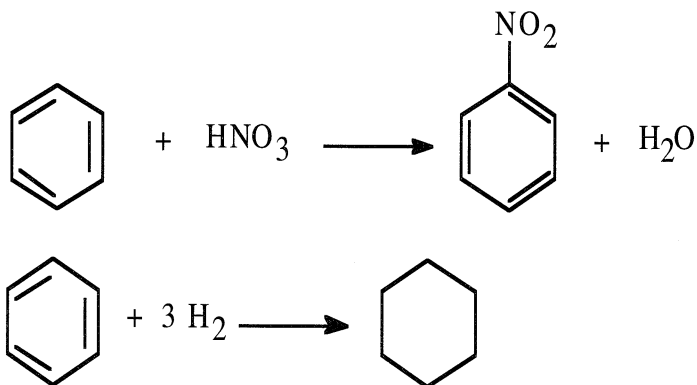
Benzene could be represented by two resonating Kekule structures.

It may also be represented as a hexagon with a circle in the middle.

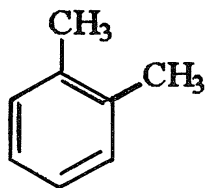
The circle is a symbol of the π cloud encircling the benzene ring. The delocalized electrons associated with the benzene ring impart very special properties to aromatic hydrocarbons. They have chemical properties of single-bond compounds such as paraffin hydrocarbons and double bond compounds such as olefins, as well as many properties of their own.

Aromatic hydrocarbons, like paraffin hydrocarbons, react by substitution, but by a different reaction mechanism and under milder conditions.

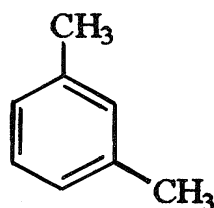
Aromatic compounds react by addition only under severe conditions. For example, electrophilic substitution of benzene using nitric acid produces nitrobenzene under normal conditions, while the addition of hydrogen to benzene occurs in presence of catalyst only under high pressure to give cyclohexane:



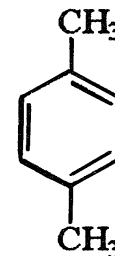
Monosubstitution can occur at any one of the six equivalent carbons of the ring. Most of the monosubstituted benzenes have common names such as toluene (methylbenzene), phenol (hydroxybenzene), and aniline (aminobenzene). When two hydrogens in the ring are substituted by the same reagent, three isomers are possible. The prefixes ortho, meta, and para are used to indicate the location of the substituents in 1,2-; 1,3-; or 1,4-positions. Forexample, there are three xylene isomers:



o-Xylene
(1,2-Dimethyl-
benzene)



m-Xylene
(1,3-Dimethyl-
benzene)



p-Xylene
(1,4-Dimethyl-
benzene)

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.

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 catcracking, and pyrolysis gasoline from steam reforming of naphtha and gas oils. As mentioned earlier, 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.

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.

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.

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.

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 cyclo-paraffins 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.

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 reformate 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.

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. Table 2-6 shows the octane rating of different hydrocarbons in the gasoline range.

Reformates are the main source for extracting C_6 - C_8 aromatics used for petrochemicals.

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.

The main constituents of kerosines obtained from atmospheric and hydrocracking units are paraffins, cycloparaffins, and aromatics. Kerosines with a high normal-paraffin content are suitable feedstocks for extracting C_{12} - C_{14} 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.

Gas Oil

Gas oil is a heavier petroleum fraction than kerosine. 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. Table 2-7 is a typical analysis of atmospheric and vacuum gas oils.

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.

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

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.

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 .

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.

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.

CHAPTER THREE

Crude Oil Processing and Production of Hydrocarbon Intermediates

INTRODUCTION

The hydrocarbon intermediates are produced by subjecting crude oils to various processing schemes. These include a primary distillation step to separate the crude oil complex mixture into simpler fractions. These fractions are primarily used as fuels. However, a small percentage of these streams are used as secondary raw materials or intermediates for obtaining olefins, diolefins, and aromatics for petrochemicals production. Further processing of these fractions may be required to change their chemical composition to the required products. These new products may also be used as fuels of improved qualities or as chemical feedstocks. For example, reforming a naphtha fraction catalytically produces a reformat rich in aromatics. The major use of the reformat is to supplement the gasoline pool due to its high octane rating. However, the reformat is also used to extract the aromatics for petrochemicals use. At this point, the production of intermediates for petrochemicals is not separable from the production of fuels.

PHYSICAL SEPARATION PROCESSES

Physical separation techniques separate a mixture such as a crude oil without changing the chemical characteristics of the components. The separation is based on differences of certain physical properties of the constituents such as the boiling and melting points, adsorption affinities on a certain solid, and diffusion through certain membranes.

The important physical separation processes are distillation, absorption, adsorption, and solvent extraction.

ATMOSPHERIC DISTILLATION

Atmospheric distillation separates the crude oil complex mixture into different fractions with relatively narrow boiling ranges. In general, separation of a mixture into fractions is based primarily on the difference in the boiling points of the components. In atmospheric distillation units, one or more fractionating columns are used.

Distilling a crude oil starts by preheating the feed by exchange with the hot product streams. The feed is further heated to about 320°C as it passes through the heater pipe (pipe still heater).

The hot feed enters the fractionator, which normally contains 30–50 fractionation trays. Steam is introduced at the bottom of the fractionator to strip off light components. The efficiency of separation is a function of the number of theoretical plates of the fractionating tower and the reflux ratio. Reflux is provided by condensing part of the tower overhead vapors. Reflux ratio is the ratio of vapors condensing back to the still to vapors condensing out of the still (distillate). The higher the reflux ratio, the better the separation of the mixture.

Products are withdrawn from the distillation tower as side streams, while the reflux is provided by returning a portion of the cooled vapors from the tower overhead condenser. Additional reflux could be obtained by returning part of the cold side stream products to the tower. In practice, the reflux ratio varies over a wide range according to the specific separations desired. From the overhead condenser, the uncondensed gases are separated, and the condensed light naphtha liquid is withdrawn to storage.

Heavy naphtha, kerosine, and gas oil are withdrawn as side stream products. Table 3-1 shows the approximate boiling ranges for crude oil fractions. The residue (topped crude) is removed from the bottom of the distillation tower and may be used as a fuel oil. It may also be charged to a vacuum distillation unit, a catalytic cracking or steam cracking process. Figure 3-1 is a flow diagram for atmospheric and vacuum distillation units.

Table 3-1
Approximate ASTM boiling point ranges for crude oil fractions

Fractions	Boiling ranges	
	°F	°C
Light naphtha	85-210	30-99
Heavy naphtha	190-400	88-204
Kerosine	340-520	171-271
Atmospheric gas oil	540-820	288-438
Vaccum gas oil	750-1050	399-566
Vaccum residue	1000+	538+