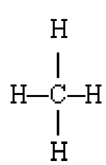
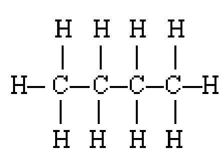
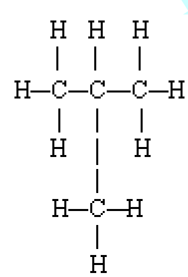
B. **BASICS OF HYDROCARBON CHEMISTRY**. Crude oil is a mixture of hydrocarbon molecules, which are organic compounds of carbon and hydrogen atoms that may include from one to 60 carbon atoms. The properties of hydrocarbons depend on the number and arrangement of the carbon and hydrogen atoms in the molecules. The simplest hydrocarbon molecule is one carbon atom linked with four hydrogen atoms: methane. All other variations of petroleum hydrocarbons evolve from this molecule. Hydrocarbons containing up to four carbon atoms are usually gases, those with 5 to 19 carbon atoms are usually liquids, and those with 20 or more are solids. The refining process uses chemicals, catalysts, heat, and pressure to separate and combine the basic types of hydrocarbon molecules naturally found in crude oil into groups of similar molecules. The refining process also rearranges their structures and bonding patterns into different hydrocarbon molecules and compounds. Therefore it is the type of hydrocarbon (paraffinic, naphthenic, or aromatic) rather than its specific chemical compounds that is significant in the refining process.

1. **Three Principal Groups or Series of Hydrocarbon Compounds that Occur Naturally in Crude Oil**.

a. **Paraffins**. The paraffinic series of hydrocarbon compounds found in crude oil have the general formula C_nH_{2n+2} and can be either straight chains (normal) or branched chains (isomers) of carbon atoms. The lighter, straight-chain paraffin molecules are found in gases and paraffin waxes. Examples of straight-chain molecules are methane, ethane, propane, and butane (gases containing from one to four carbon atoms), and pentane and hexane (liquids with five to six carbon atoms). The branched-chain (isomer) paraffins are usually found in heavier fractions of crude oil and have higher octane numbers than normal paraffins. These compounds are saturated hydrocarbons, with all carbon bonds satisfied, that is, the hydrocarbon chain carries the full complement of hydrogen atoms.

TYPICAL PARAFFINS.

Example of simplest HC molecule (CH_4):	Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula (C_4H_{10}):	
METHANE (CH_4)	BUTANE (C_4H_{10})	ISOBUTANE (C_4H_{10})
		

b. **Aromatics** are unsaturated ring-type (cyclic) compounds which react readily because they have carbon atoms that are deficient in hydrogen. All aromatics have at least one benzene ring (a single-ring compound characterized by three double bonds alternating with three single bonds between six carbon atoms) as part of their molecular structure. Naphthalenes are fused double-ring aromatic compounds. The most complex aromatics, polynuclears (three or more fused aromatic rings), are found in heavier fractions of crude oil.

c. **Naphthenes** are saturated hydrocarbon groupings with the general formula C_nH_{2n}, arranged in the form of closed rings (cyclic) and found in all fractions of crude oil except the very lightest. Single-ring naphthenes (monocycloparaffins) with five and six carbon atoms predominate, with two-ring naphthenes (dicycloparaffins) found in the heavier ends of naphtha.

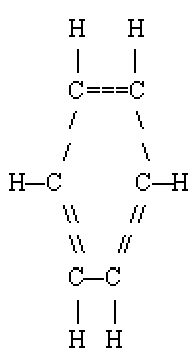
2. **Other Hydrocarbons**.

a. **Alkenes** are mono-olefins with the general formula C_nH_{2n} and contain only one carbon-carbon double bond in the chain. The simplest alkene is ethylene, with two carbon atoms joined by a double bond and four hydrogen atoms. Olefins are usually formed by thermal and catalytic cracking and rarely occur naturally in unprocessed crude oil.

FIGURE. TYPICAL AROMATICS.

Example of simple aromatic compound:

BENZENE (C_6H_6)



Examples of simple double-ring aromatic compound:

NAPTHALENE ($C_{10}H_8$)

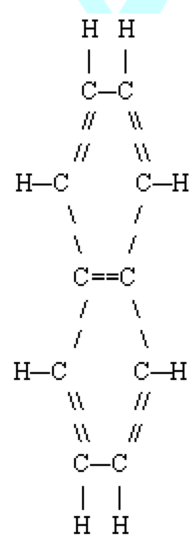


FIGURE : TYPICAL NAPHTHENES.

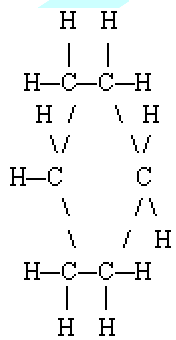
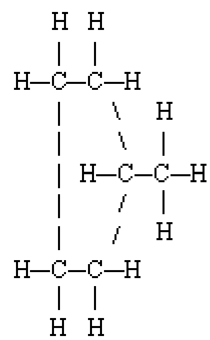
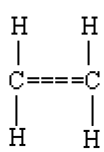
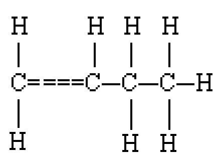
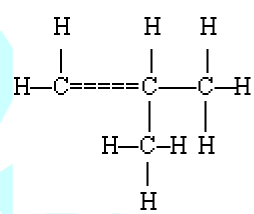
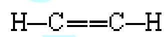
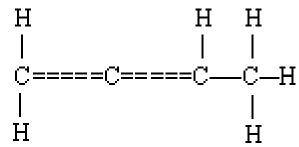
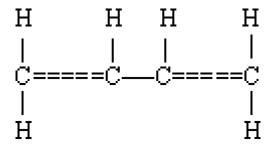
Example of typical single-ring naphthene:	Examples of naphthene with same chemical formula (C_6H_{12}) but different molecular structure:
CYCLOHEXANE (C_6H_{12})	METHYL CYCLOPENTANE (C_6H_{12})
	

FIGURE : TYPICAL ALKENES.

Simplest Alkene (C_2H_4):	Typical Alkenes with the same chemical formula (C_4H_8) but different molecular structures:	
ETHYLENE (C_2H_4)	1-BUTENE (C_4H_8)	ISOBUTENE (C_4H_8)
		

3. **Dienes and Alkynes**. Dienes, also known as diolefins, have two carbon-carbon double bonds. The alkynes, another class of unsaturated hydrocarbons, have a carbon-carbon triple bond within the molecule. Both these series of hydrocarbons have the general formula C_nH_{2n-2}. Diolefins such as 1,2-butadiene and 1,3-butadiene, and alkynes such as acetylene, occur in C_5 and lighter fractions from cracking. The olefins, diolefins, and alkynes are said to be unsaturated because they contain less than the amount of hydrogen necessary to saturate all the valences of the carbon atoms. These compounds are more reactive than paraffins or naphthenes and readily combine with other elements such as hydrogen, chlorine, and bromine.

FIGURE :TYPICAL DIOLEFINS AND ALKYNES.

Simplest Alkyne: (C_2H_2):	Typical Diolefins with the same chemical formula (C_4H_6) but different molecular structures:	
ACETYLENE (C_2H_2)	1,2-BUTADIENE (C_4H_6)	1,3-BUTADIENE (C_4H_6)
		

Nonhydrocarbons.

a. **Sulfur Compounds**. Sulfur may be present in crude oil as hydrogen sulfide (H_2S), as compounds (e.g. mercaptans, sulfides, disulfides, thiophenes, etc.) or as elemental sulfur. Each crude oil has different amounts and types of sulfur compounds, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans. Moreover, the corrosive sulfur compounds have an obnoxious odor. Pyrophoric iron sulfide results from the corrosive action of sulfur compounds on the iron and steel used in refinery process equipment, piping, and tanks. The combustion of petroleum products containing sulfur compounds produces undesirables such as sulfuric acid and sulfur dioxide. Catalytic hydrotreating processes such as hydrodesulfurization remove sulfur compounds from refinery product streams. Sweetening processes either remove the obnoxious sulfur compounds or convert them to odorless disulfides, as in the case of mercaptans.

b. **Oxygen Compounds**. Oxygen compounds such as phenols, ketones, and carboxylic acids occur in crude oils in varying amounts.

c. **Nitrogen Compounds**. Nitrogen is found in lighter fractions of crude oil as basic compounds, and more often in heavier fractions of crude oil as nonbasic compounds that may also include trace metals such as copper, vanadium, and/or nickel. Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

d. **Trace Metals**. Metals, including nickel, iron, and vanadium are often found in crude oils in small quantities and are removed during the refining process. Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts.

e. **Salts**. Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine). These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling. Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when crude is heated. Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH_4Cl), which causes fouling and corrosion.

f. **Carbon Dioxide**. Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

g. **Naphthenic Acids**. Some crude oils contain naphthenic (organic) acids, which may become corrosive at temperatures above 450° F when the acid value of the crude is above a certain level