Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering

Department

Petroleum Refining Processes

Fourth Class

Lecture 1

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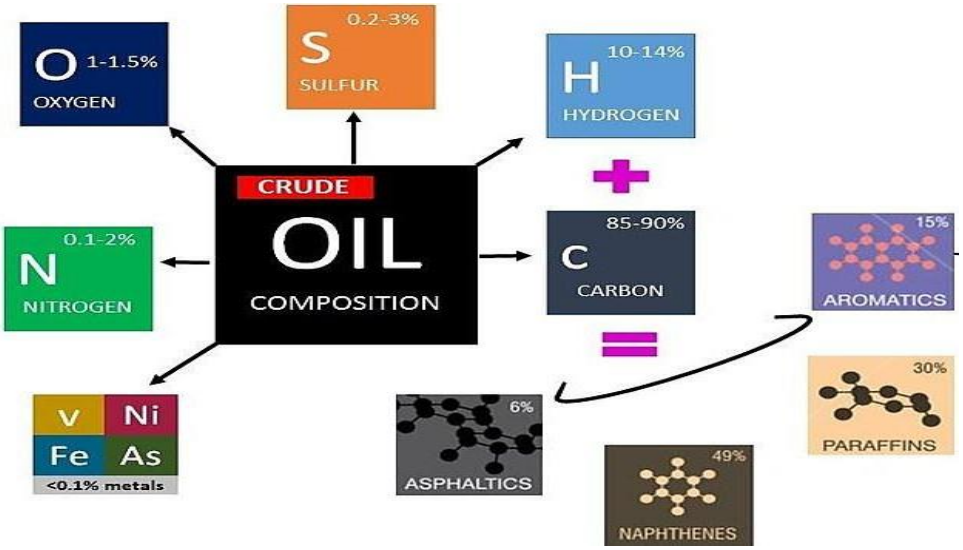
Introduction

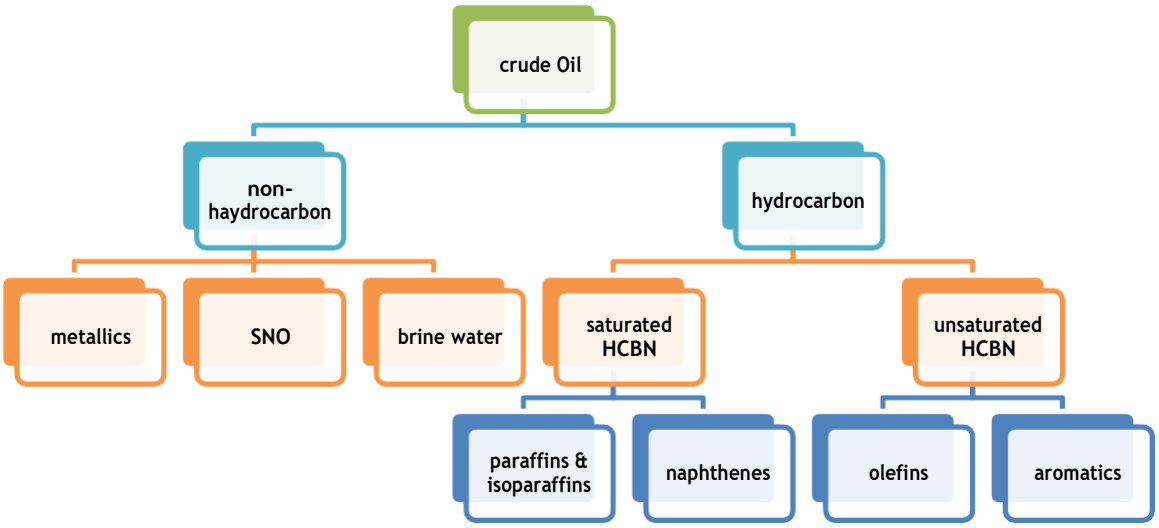
Petroleum refining plays an important role in our lives. Most transportation vehicles are powered by refined products such as gasoline, diesel, aviation turbine kerosene (ATK) and fuel oil. Petroleum has remained an important aspect of our lives and will do so for the next four or five decades. The fuels that are derived from petroleum supply more than half of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity. Petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry.

Composition and Classification of Crude Oils

Crude oil is a complex liquid mixture made up of a vast number of **hydrocarbon compounds** that consist mainly of carbon and hydrogen in differing proportions. In addition, small amounts of **organic compounds** containing **sulfur, oxygen, nitrogen and metals such as vanadium, nickel, iron and copper** are also present.



Crude Oil Chemical Composition Chart:

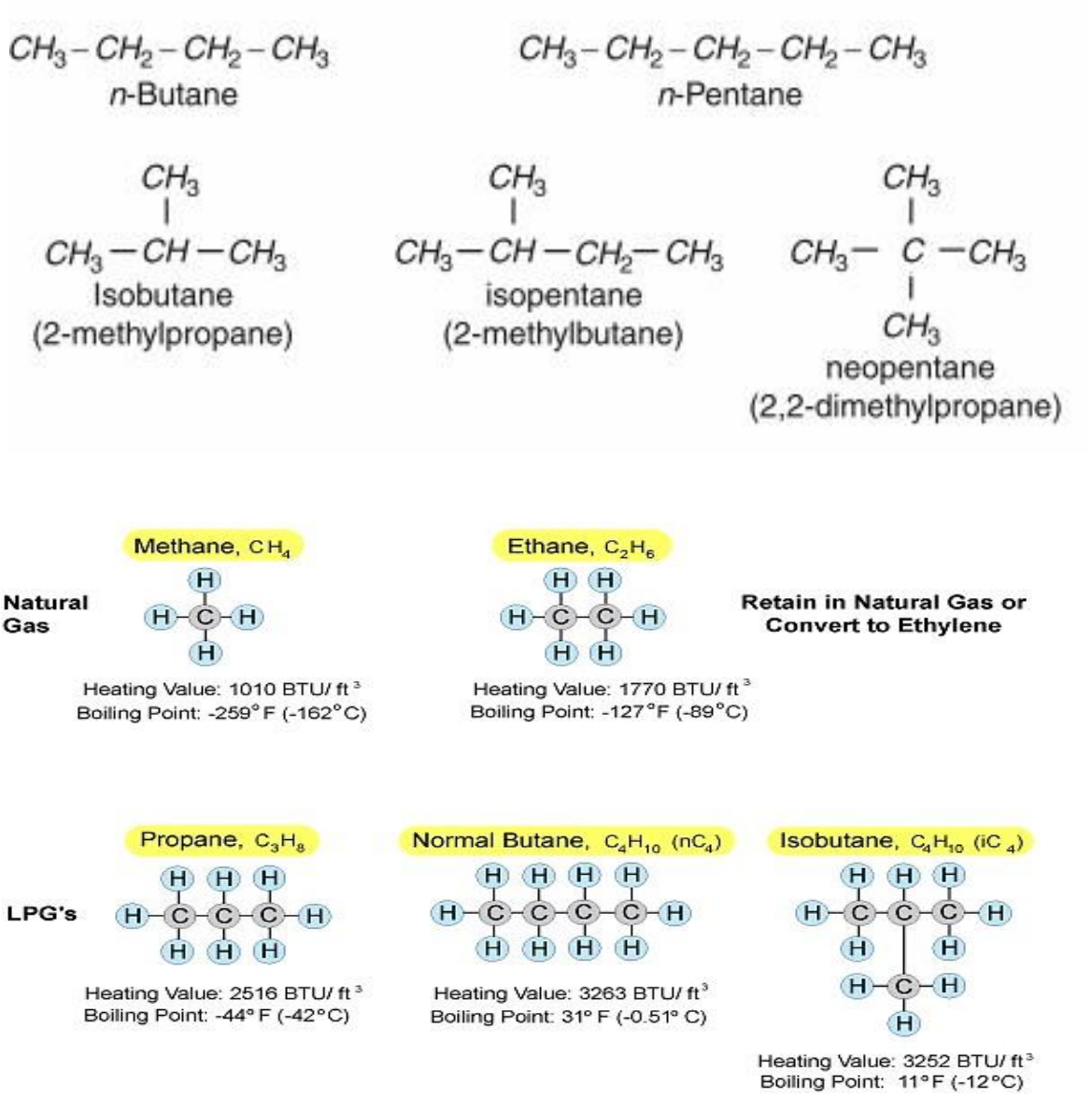


Hydrocarbon Components:

There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present. These classes are:

- **Saturated hydrocarbons** contain only carbon–carbon single bonds. They are known as paraffins (or alkanes), or naphthenes (or cycloalkanes) if they are cyclic.

- **Paraffins & Isoparaffins** (or alkanes) if they are acyclic. General formula: **(C_nH_{2n+2})** (n is a whole number, usually from 1 to 20), Paraffins could be normal alkanes (n-alkanes, n-paraffins) or branched isoparaffins, can be gasses or liquids at room temperature depending upon the molecule. For example, methane, ethane, propane, butane, isobutane, pentane, hexane. The presence of isoparaffins in gasoline is essential for increasing the octane number of gasoline fuels.

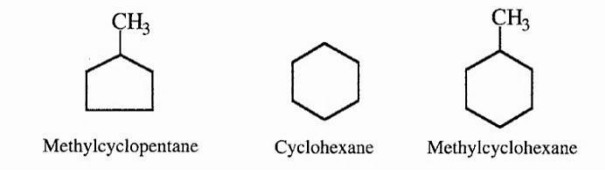


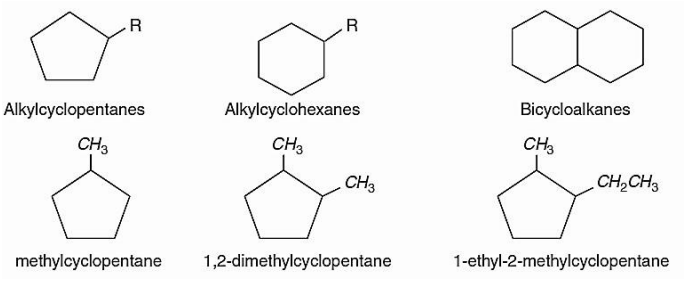
Paraffins are: High molecular weight, High boiling point and Low octane number.

Isoparaffins are: low boiling points and high octane.

- **Naphthenes** (or cycloalkanes):

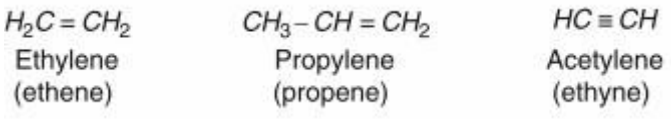
  General formula: CnH2n (n is a whole number usually from 1to 20), ringed structures with one or more rings, rings contain only single bonds between the carbon atoms, typically liquids at room temperature. For example: cyclohexane (C_6H_{12}).





- **Unsaturated hydrocarbons** contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as olefins. Those that contain a carbon–carbon double bond are called alkenes, while those with carbon–carbon triple bond are alkyenes.
- **Olefins (also known as alkenes):**

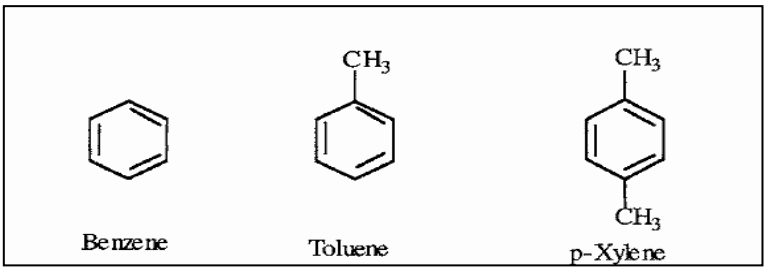
General formula: CnH2n (n is a whole number, usually from 1 to 20), linear or branched chain molecules containing one carbon-carbon double-bond, can be liquid or gas. For example: ethylene, butene, isobutene.



- **Aromatic hydrocarbons** are special class of cyclic compounds related in structure to benzene. General formula: C6H5 - Y (Y is a longer, straight molecule that connects to the benzene ring), ringed structures with one or more rings, rings contain six carbon atoms, with alternating double and single bonds between the carbons, typically liquids.

Crude oils from various origins contain different types of aromatic compounds in different concentrations. Light petroleum fractions contain mono-aromatics rings such as benzene, Toluene and Xylene, which have one benzene ring with one or more of the hydrogen atoms substituted by another atom or alkyl groups. Examples of these compounds are toluene and xylene.

BTX is important petrochemical feed stocks, and their presence in gasoline increases the octane number.



More complex aromatic compounds consist of a number of benzene rings. These are known as polynuclear aromatic compounds. They are found in the heavy petroleum cuts, and their presence is undesirable because they cause **catalyst deactivation** and coke deposition during processing, besides causing **environmental problems** when they are present in diesel and fuel oils.

Non-hydrocarbon Components

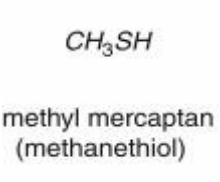
1. Sulfur Compounds:

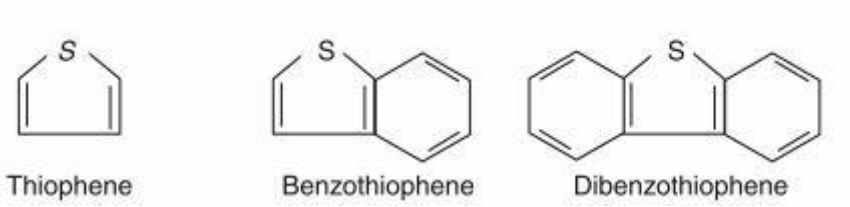
- The Sulfur content of crude oils varies from less than 0.05 to more than 10 wt% but generally falls in the range 1–4 wt%. Crude oil with **less than 1 wt %** sulfur is referred to as **low sulfur or sweet**, and that with **more than 1 wt%** sulfur is referred to as **high sulfur or sour**.
- Crude oils contain sulfur heteroatoms in the form of elemental sulfur S, dissolved hydrogen sulphide H2S, carbonyl sulphide COS, inorganic forms and most importantly organic forms, in which sulfur atoms are positioned within the organic hydrocarbon molecules.

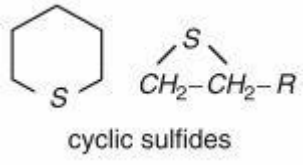
Disadvantages of Sulphur components:

- Sulfur compounds lead to environmental pollution (their emissions are very dangerous to human safety and environment).
- decreases the life of machinery.
- Corrode the metallic parts of the internal combustion engine, pipes, machines and equipment.
- Reduce octane number.
- Reduce the activity of Tetra Ethyl Lead (TEL) added to gasoline.
- Causes solid depositions (cause catalyst poisoning and reduce the catalyst activity).
- Reduce oxidation resistance.

Sulfur containing constituents of crude oils vary from simple mercaptans, also known as thiols, to sulphides and polycyclic sulphides (Mercaptans (R–SH), sulphides (R–S–R'), disulphides (R–S–S–R'), Thiophenes)

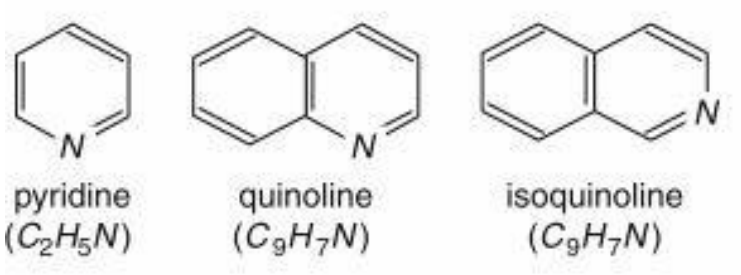






2. Nitrogen Compounds

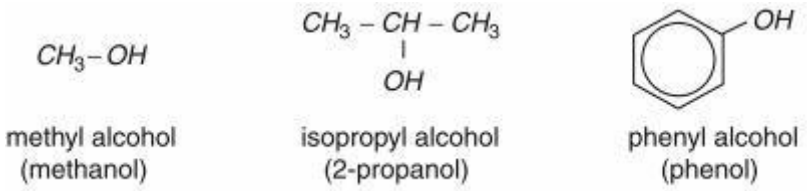
- Crude oils contain very low amounts of nitrogen compounds **(0.1-0.9 wt%) less than 1 wt%.**
- In general, the more asphaltic the oil, the higher its nitrogen content. Nitrogen compounds are more stable than Sulphur compounds and therefore are harder to remove.
- The nitrogen compounds in crude oils may be classified as basic or non-basic. Basic nitrogen compounds consist of pyridines. The greater part of the nitrogen in crude oils is the non-basic nitrogen compounds, which are generally of pyrrole types.



- The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.
- Nitrogen compounds have great significance in refinery operations. They can be responsible for the poisoning of a cracking catalyst, increases carbon residue, decreases API and they also contribute to gum formation in finished products.
- Nitrogen compounds are concentrated in heavier petroleum fractions and residues.

3. Oxygen Compounds

- **The oxygen content of crude oil is usually less than 2% wt.** A phenomenally high oxygen content indicates that the oil has suffered prolonged exposure to the atmosphere
- Oxygen compounds include alcohols, ethers, carboxylic acids, phenolic compounds, ketones, esters and anhydrides
- The presence of such compounds causes the crude to be acidic with consequent processing problems such as corrosion.



4. Metallic components:

- Organic metallic (Iron Fe, Nickel Ni, Vanadium V, Cadmium Cd).
- Soap metallic (Magnesium Mg, Calcium Ca).
- Salt metallic (Na^+ and Ba^{2+}).

Disadvantages:

1- Effect on catalyst activity.

2- Coke formation.

3- Reduce the yield of the gasoline.

4- Form ash deposits-power generation plants.

5- Corrosion.

5. Brine water:

Water molecules are suspension in crude oil with extremely high concentrations of dissolved salt ions nearly 300 – 300 000 ppm. The ions are divided into two types:

1. Positive ions (Na^{+}, Ba2+, Mg2+, Al3+…etc)
2. Negative ions (Cl^{-} , Br^{-} , SO_4^{-2}, I^{-}…etc).

6. Asphaltenes and Resins Compounds:

Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They are made up of condensed polynuclear aromatic layers linked by saturated links. The presence of high amounts of asphaltenes in crude oil can create tremendous problems in production because they tend to precipitate inside the pores of rock formations, well heads and surface processing equipment's. They may also lead to transportation problems because they contribute to gravity and viscosity increases of crude oils. Resins are polar molecules have high molecular weight, which are insoluble in liquid propane but soluble in n-heptane. It is believed that the resins are responsible for dissolving and stabilizing the solid asphaltenes molecules in petroleum.