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 (See Table below).

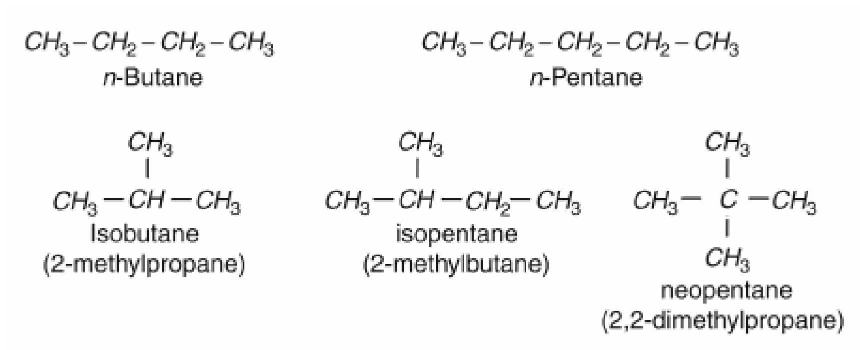
Element	Composition (wt%)
Carbon	83.0–87.0
Hydrogen	10.0–14.0
Sulphur	0.05–6.0
Nitrogen	0.1–0.2
Oxygen	0.05–2.0
Ni	<120 ppm
V	<1200 ppm

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) if they are acyclic, or naphthenes (or cycloalkanes) if they are cyclic.
- 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.
- Aromatic hydrocarbons are special class of cyclic compounds related in structure to benzene.

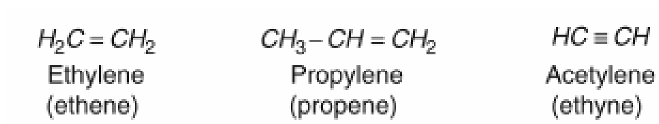
1- Paraffins

General formula: C_nH_{2n+2} (n is a whole number, usually from 1 to 20), straight or branched-chain molecules, can be gasses or liquids at room temperature depending upon the molecule. For example, methane, ethane, propane, butane, isobutane, pentane, hexane



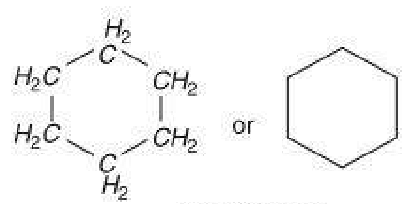
2- Olefins (also known as alkenes)

General formula: C_nH_{2n} (n is a whole number, usually from 1 to 20), linear or branched chain molecules containing one carboncarbon double-bond, can be liquid or gas. For example: ethylene, butene, isobutene



3- Naphthenes (cycloalkanes)

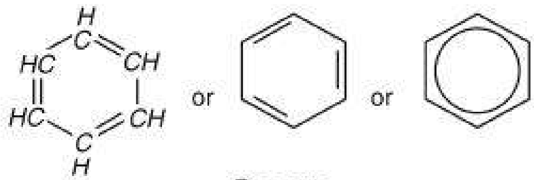
General formula: C_nH_{2n} (n is a whole number usually from 1to 20), ringed structures with one or more rings, rings contain only single bonds between the carbon atoms, typically liquids at room temperature. For example: cyclohexane, methyl cyclopentane



Cyclohexane

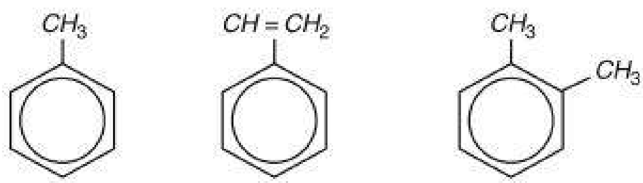
4- Aromatics

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. For examples benzene, naphthalene



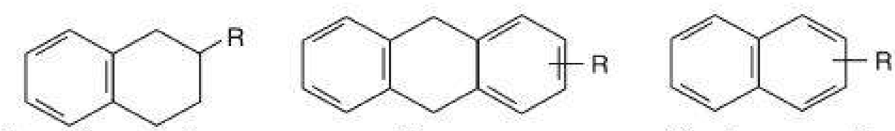
Benzene

Crude oils from various origins contain different types of aromatic compounds in different concentrations. Light petroleum fractions contain mono-aromatics, 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.

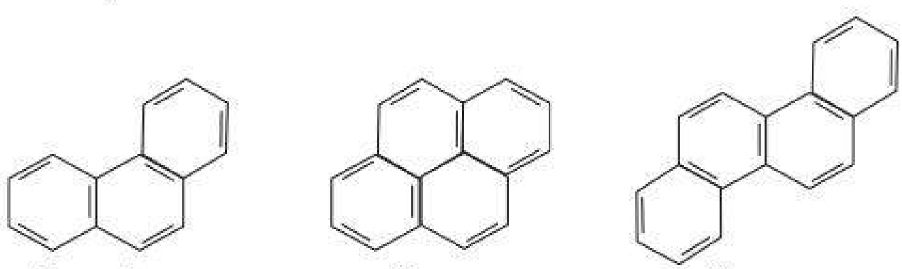


Toluene (methylbenzene) Styrene o-xylene (1,2-Dimethylbenzene)

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. Examples of polynuclear aromatic compounds are shown below.



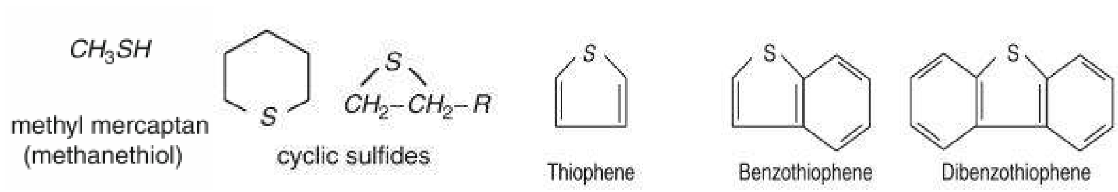
Aromatic-cycloalkanes Fluorenes Binuclear aromatics



Phenanthrene Pyrene Chrysene

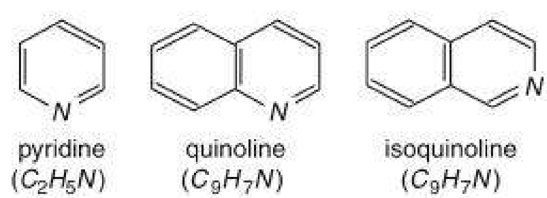
5- Sulfur Compounds

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 H_2S, carbonyl sulphide COS, inorganic forms and most importantly organic forms, in which sulfur atoms are positioned within the organic hydrocarbon molecules. Sulfur compounds lead to environmental pollution, decreases the life of machinery, corrodes of pipes, machines and equipment, affecting the additives used for the purpose of increasing the octane number, reduce the activity of Tetra Ethyl Lead (TEL) added to gasoline. As a result, the engine metal will erode and leads to destruct the metallic parts. Also, their emissions are very dangerous to human safety and environment. In addition, these impurities cause catalyst poisoning and reduce the catalyst activity. 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)



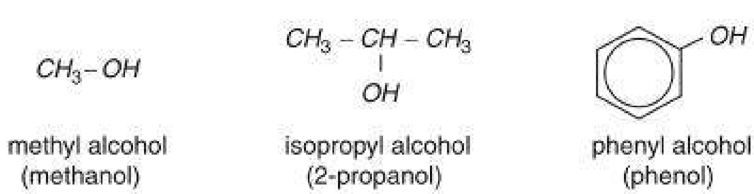
6-Nitrogen Compounds

Crude oils contain very low amounts of nitrogen compounds, less than 1%, 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.



7- Oxygen Compounds

Less than 1% (found in organic compounds such as carbon dioxide, phenols, ketones, carboxylic acids) occur in crude oils in varying amounts.



8- Metals Compounds

Metallic compounds exist in all crude oil types in very small amounts. Their concentration must be reduced to avoid operational problems and to prevent them from contaminating the products. Metals affect many upgrading processes. They cause poisoning to the catalysts used for hydroprocessing and cracking. Even minute amounts of metals (iron, nickel and vanadium) in the feedstock to the catalytic cracker affect the activity of the catalyst and result in increased gas and coke formation and reduced gasoline yields. 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.

9- Asphaltenes and Resins Compounds

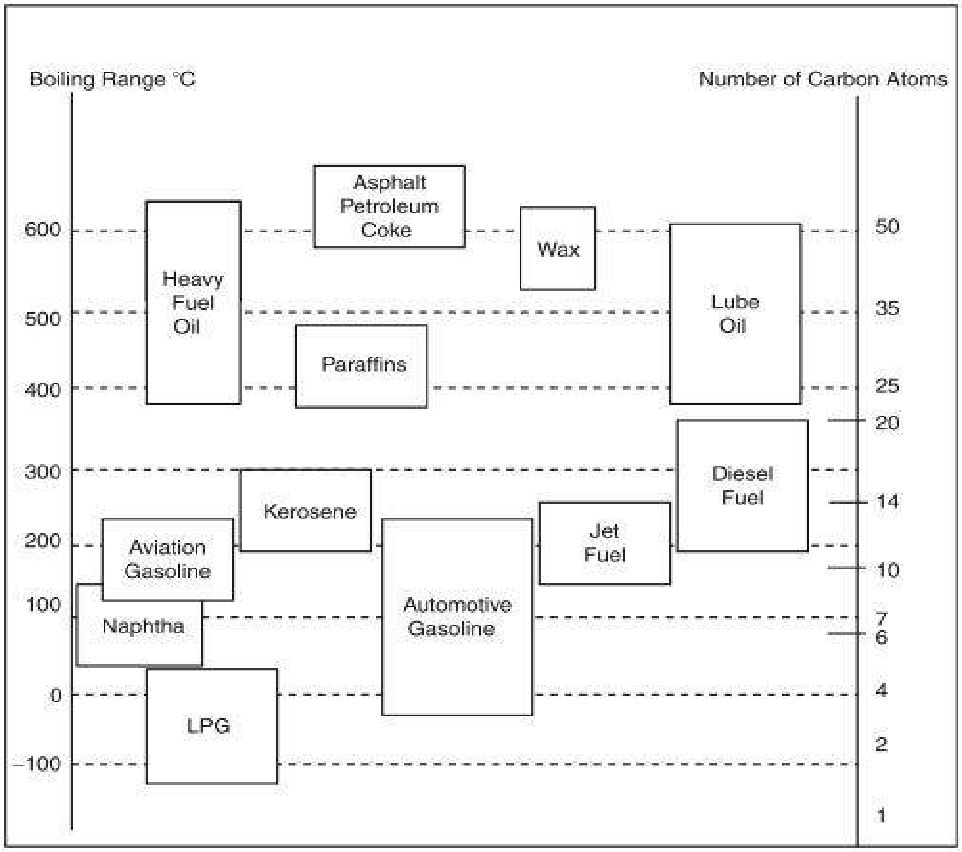
Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They are made up of condensed polynuclear aromatic layers linked by saturated links. The presence of high amounts of asphaltenes in crude oil can create tremendous problems in production because they tend to precipitate inside the pores of rock formations, well heads and surface processing equipments. 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 asphaltene molecules in petroleum.

Products Composition

To understand the diversity contained in crude oil, and to understand why refining crude oil is important in our society, look through the following list of products that come from crude oil:

- **Liquefied Petroleum Gas (LPG)**
    - used for heating, cooking, making plastics
    - small alkanes (1 to 4 carbon atoms)
    - commonly known by the names methane, ethane, propane, butane
    - boiling range < 90 degrees Fahrenheit / < 27 degrees Celsius
    - often liquified under pressure to create LPG (liquefied petroleum gas)
- **Gasoline**
    - motor fuel
    - liquid
    - mix of alkanes and cycloalkanes (5 to 7 carbon atoms)
    - boiling range = 90-220 degrees Fahrenheit / 27-93 degrees Celsius
- **Kerosene**
    - fuel for jet engines and tractors; starting material for making other products
    - liquid
    - mix of alkanes (10 to 15 carbons) and aromatics
    - boiling range = 315-450 degrees Fahrenheit / 177-293 degrees Celsius
- **Diesel Fuel**
    - used for diesel fuel and heating oil, starting material for making other products
    - liquid
    - alkanes containing 13-18 carbon atoms
    - boiling range = 450-650 degrees Fahrenheit / 293-315 degrees Celsius
- **Lubricating oil**
    - used for motor oil, grease, other lubricants
    - liquid
    - long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, aromatics
    - boiling range = 572 to 700 degrees Fahrenheit / 300 to 370 degrees Celsius
- **Fuel oil**
    - used for industrial fuel; starting material for making other products
    - liquid
    - long chain (16 to 40 carbon atoms) alkanes, cycloalkanes, aromatics
    - boiling range = 650-800 degrees Fahrenheit / 315-565 degrees Celsius
- **Residual oil**
    - coke, asphalt, tar, waxes; starting material for making other products
    - solid
    - multiple-ringed compounds with 40 or more carbon atoms
    - boiling range = greater than 800 degrees Fahrenheit / 565 degrees Celsius



Evaluation of Crude Oils

Base of Crude Oil

The crude oil can be classified into:
1) Paraffinic base crude (P)
2) Intermediate bas crude (IN)
3) Naphthenic base crude (N)

Classification Methods

1- Composition of Residue

$paraffin \rangle 5\% \rightarrow P$

$2-5\% paraffin \rightarrow IN$

$parrafin \langle 2\% \rightarrow N$

2- Sp.gr of two cuts.

API fraction 1	API fraction 2	Crude Base
≥ 40	≥ 30	P
33 - 40	20 - 30	IN
≤ 33	≤ 20	N
≥40	20 - 30	PIN (mix)
30 - 40	≥ 30	INP (mix)

3- Watson Factor (Kw)

$$K_W = \frac{(1.8T_b)^{1/3}}{SG}$$

Where
Tb = mean average boiling point (MeABP) K
SG = specific gravity at 15.5°C

Kw	Crude Base
10.5 - 11.5	P
11.5 – 12.1	IN
12.1 – 12.5	N
12.08	NIN
11.47	PIN

4- Correlation index (CI)

$$CI = \frac{87552}{T_b} + 473.7SG - 456.8$$

CI	Crude Base
0 – 15	P
15 – 50	IN
50 - 00	N

5- Viscosity Gravity Constant (VGC)

$$VGC = \frac{10SG - 1.0752 \log_{10}(V_{38} - 38)}{10 - \log_{10}(V_{38} - 38)}$$

$$VGC = \frac{SG - 0.24 - 0.022 \log_{10}(V_{99} - 35.5)}{0.755}$$

Where
V_{38} = viscosity at 38°C (100F in SUS (Saybolt Universal Seconds)
V_{99} = Saylbolt viscosity (SUS) at 99°C (210F)

VGC	Crude Base
< 0.82	P
0.82 – 0.9	IN
> 0.9	N