Petroleum Chemistry

3rd stage (2022-2023)

Chemistry Department

Dr. Sangar Salih Ahmed

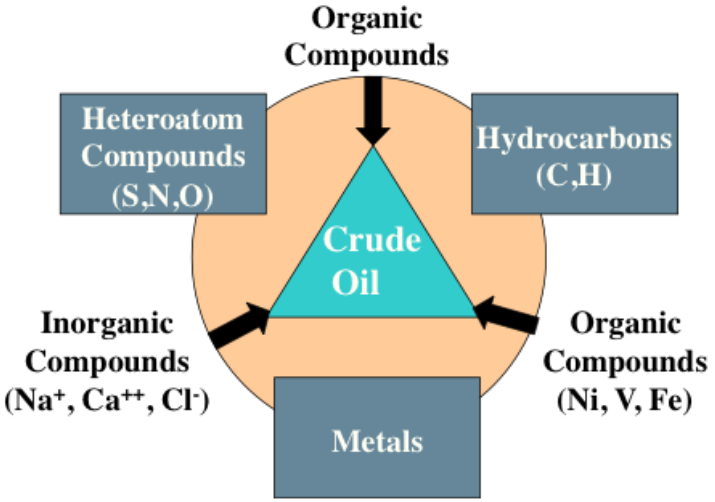
Course Outline

- ***Introduction to crude oil.***
- **Composition and classification of crude oil.**
- **Testing and evaluation of crude oil.**
- **Pretreatment and distillation of crude oil.**
- **Products from crude oil.**

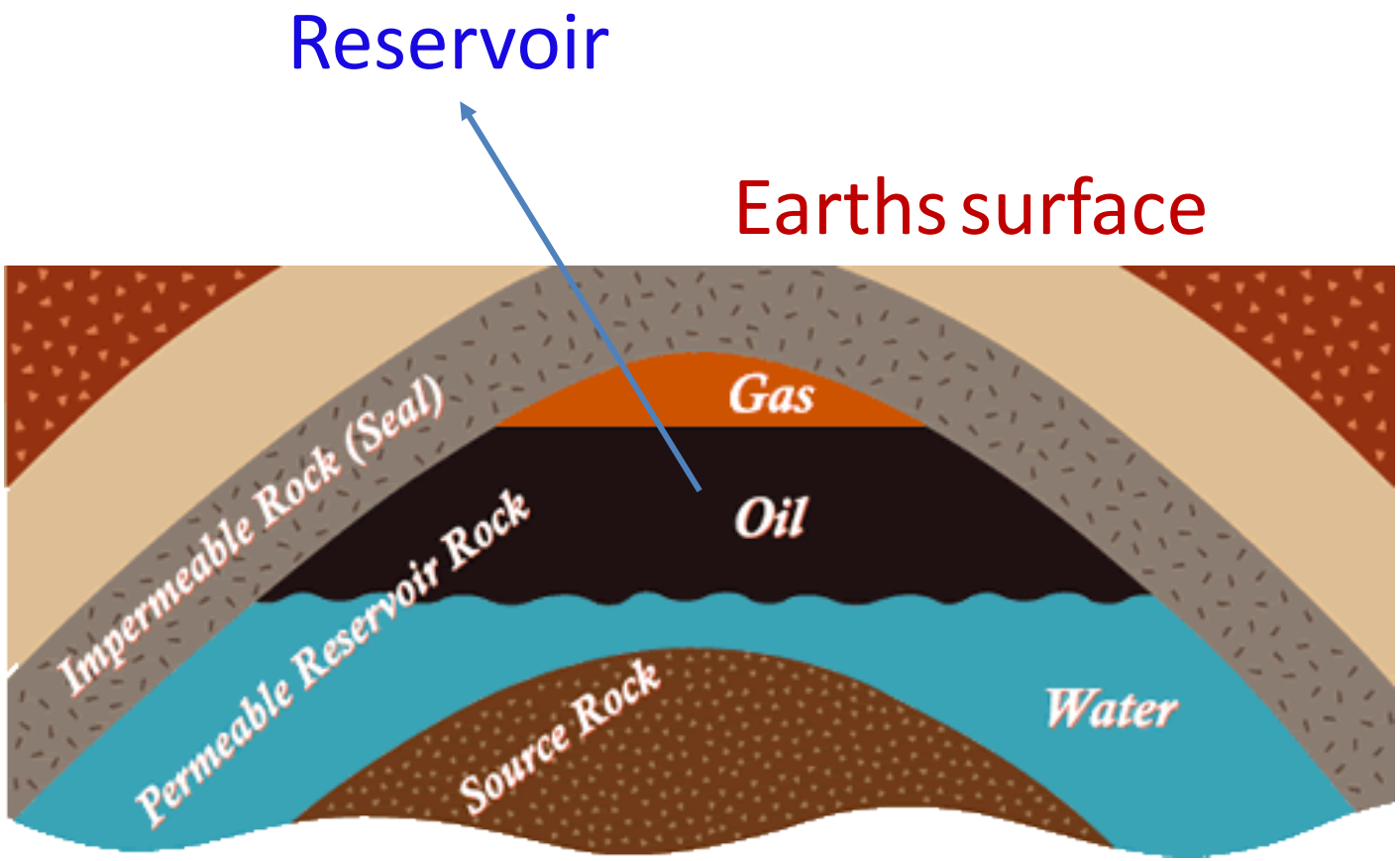
INTRODUCTION

Petroleum is a Latin word and is considered as made up of *petra* meaning rock and *oleum* meaning oil.

Crude oil or Petroleum is a naturally occurring, flammable liquid "brown to black with an unpleasant smell" consisting of a complex mixture of hydrocarbons (gas, Liquid, and solid) mixed with variable amounts of sulfur, nitrogen, oxygen compounds, and trace amounts of metals such as iron, nickel, copper and vanadium. *It is often referred to as the "black gold".*



Crude oils are principally found in oil reservoirs associated with sedimentary rocks beneath the earth's surface.



Origin of Petroleum

There are two theories that support the origin of petroleum. First, the biogenic theory, which implies that petroleum made by the fossils of animals and plants from thousands years ago. Many geologists believe that petroleum is created by the remains of plants and animals that slowly decay under layers of rock. Second, the a biogenic theory which implies that carbon was present before human life on Earth. The discovery of methane supports the a biogenic theory strongly.

1-A BIOGENIC ORIGIN:

A- Marcellin Berthelot:

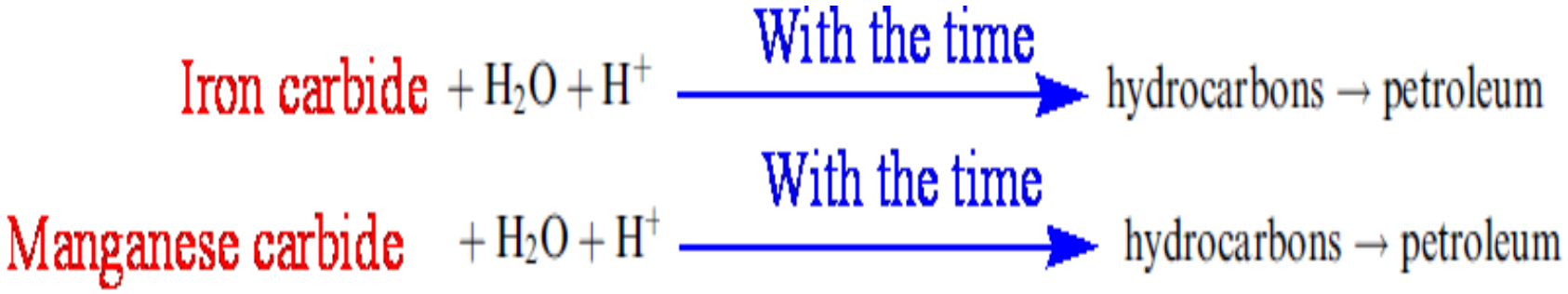
In 1866, Berthelot considered that acetylene was the basic material. Large quantities of acetylene were assumed to be produced by the reaction of water with carbides which, themselves, were formed by the reaction of alkali metals with carbonates. The conversion of acetylene to petroleum was accomplished at an elevated temperature and pressure.

$$CaCO_3 + \text{alkali metal} \rightarrow CaC_2 \text{ (calcium carbide)}$$

$$CaC_2 + H_2O \rightarrow HC \equiv CH \text{ (acetylene)} \rightarrow \text{petroleum}$$

B- Dmitri Mendele'ev:

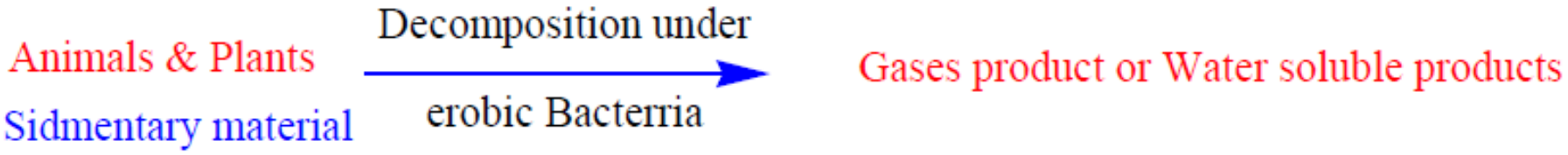
In 1902, Dmitri Mendele'ev proposed that the action of dilute acids or hot water on mixed iron and manganese carbides produces a mixture of hydrocarbons from which petroleum evolved, described another theory in which acetylene is considered to be the basic material:



2-BIOGENIC ORIGIN:

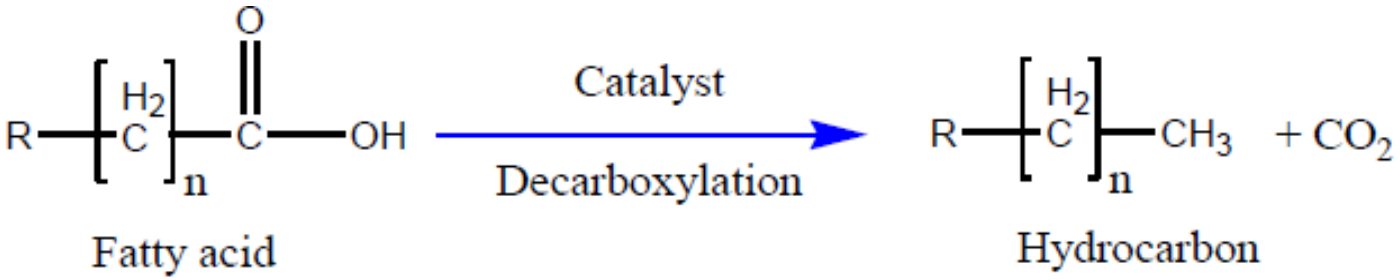
In 1911, *Engler* was the first author to postulate that an organic substance other than coal was the source material of petroleum; he invoked the concept of three separate development stages.

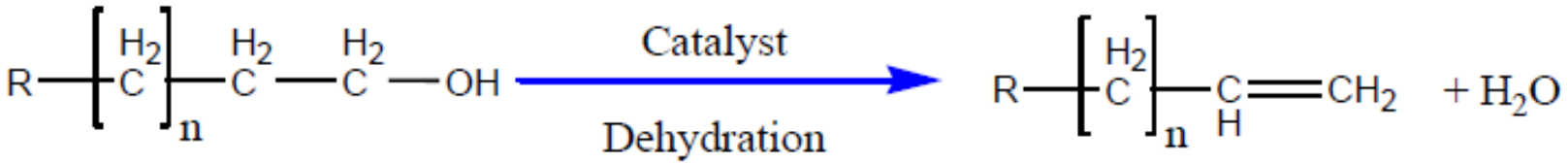
First Stage: Animal and vegetable deposit accumulate on the bottom of inland seas and are then decomposed by bacteria; the carbohydrates and the bulk of the protein are converted into water-soluble material or gases and thus removed from the site. The fats, waxes, and other fat-soluble and stable materials (resins, cholesterol, and others) remain.



Second stage: High temperatures and pressures cause carbon dioxide to evolve from compounds containing a carboxyl group, and water is produced from the hydroxy-acids and alcohols to leave a bituminous residue.

Continued application of the heat and pressure causes light cracking, producing a liquid product with a high olefin content(protopetroleum).



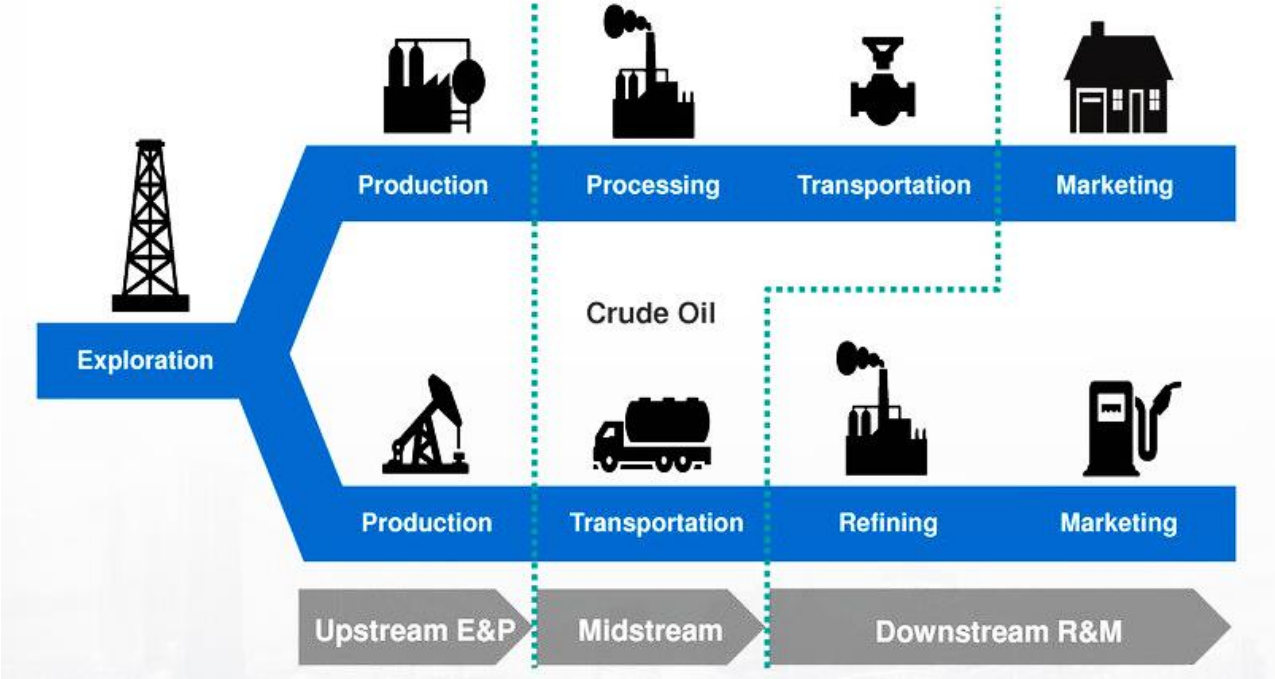


Third stage: The unsaturated components of the protopetroleum are polymerized under the influence of contact catalysts and thus the polyolefins are converted into paraffins and/or cycloparaffins (naphthenes).

Aromatics were presumed to be formed either directly during cracking, by cyclization through condensation reactions, or even during the decomposition of protein.

Petroleum Industry

The petroleum industry includes the global processes of exploration, extraction, refining, transporting (pipeline, oil tanker/barge, truck, and rail), and marketing petroleum products. The industry is usually divided into three major components: upstream, midstream, and downstream.



Petroleum Industry

Upstream: usually includes exploration, development, and production of crude oil and natural gas.

Midstream: activities can include processing, storage, and transportation of crude oils and natural gas.

Downstream: activities usually include refining/ hydrocarbon processing, marketing, and distribution.

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Composition of crude oil

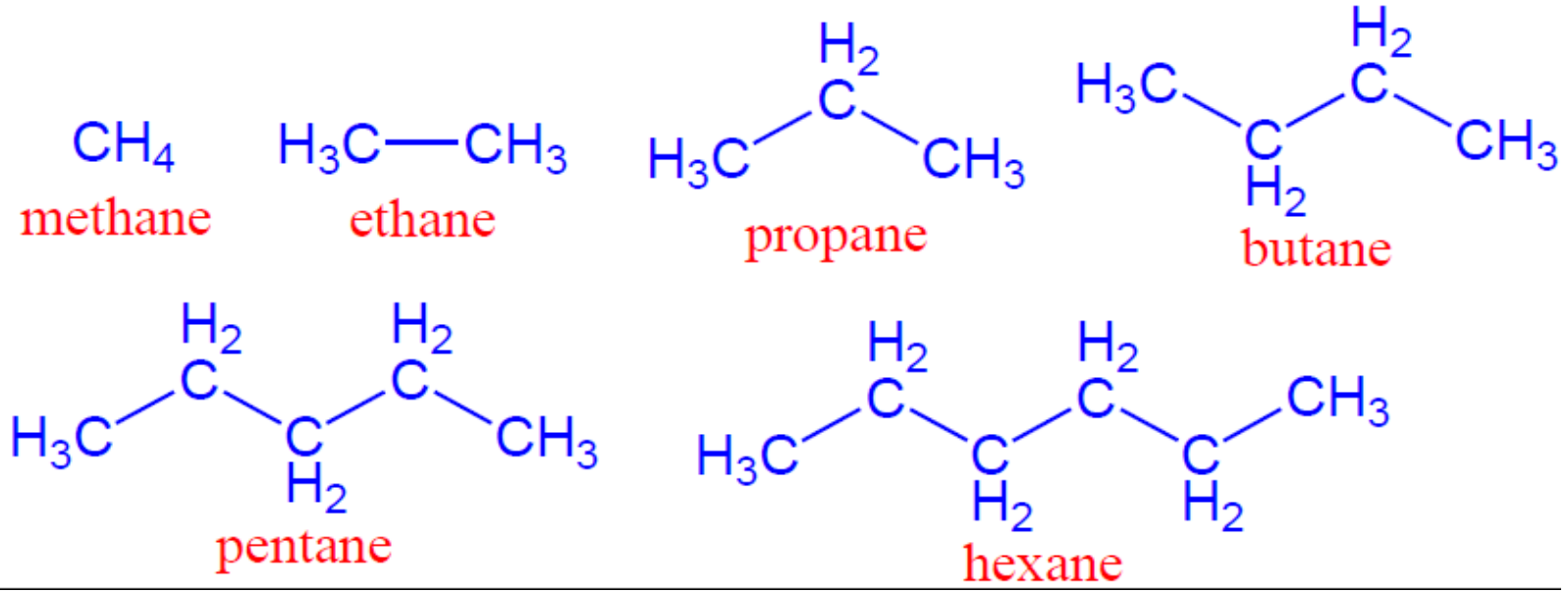
The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium.

Element	Percent range
Carbon	83 to 87%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.1 to 1.5%
Sulfur	0.5 to 6%
Metals	less than 1000 ppm

Chemical composition of crude oil:

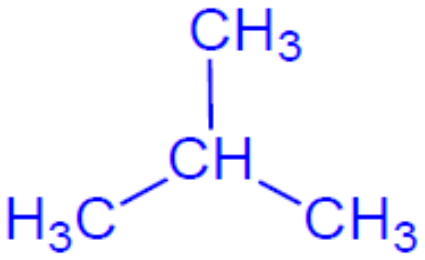
1.1. A-Alkanes (Paraffins):

Normal alkanes (n-paraffins: are straight-chain hydrocarbons having no branches) are saturated hydrocarbons having the general formula C_nH_{2n+2}. Methane, ethane, propane, and butane are gaseous hydrocarbons.

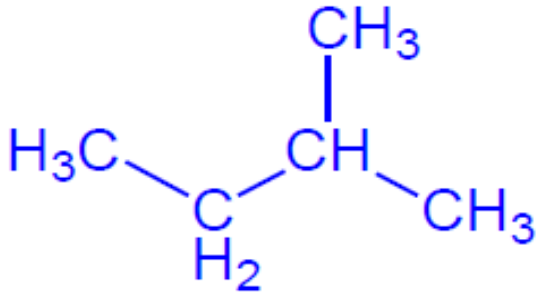


B- Isoparaffin:

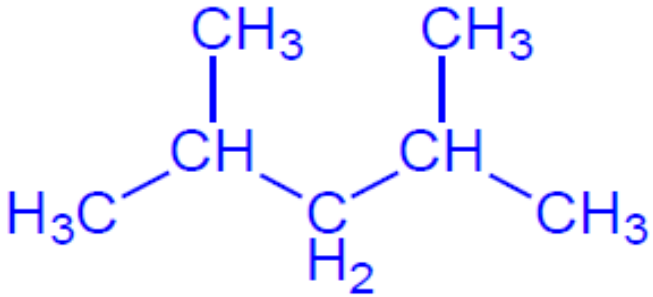
An isoparaffin is an isomer having a methyl group branching from carbon number 2 of the main chain. Crude oils contain many short, medium, and long-chain normal and branched paraffins.



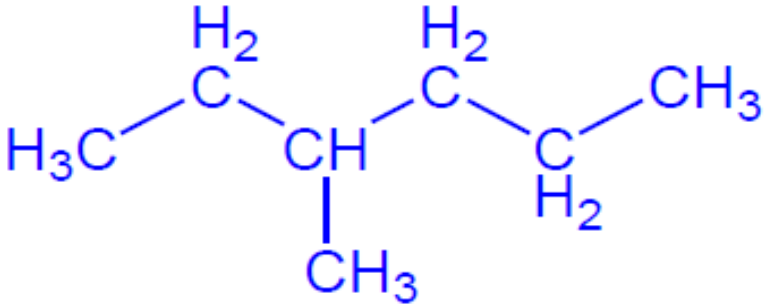
isobutane



isopentane



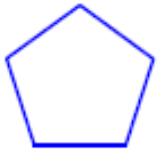
2,4-dimethylpentane



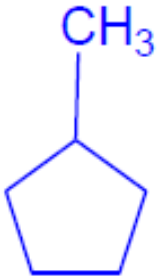
3-methylhexane

1.2.Saturated cyclic hydrocarbons: (Or Cycloparaffins or Naphthenes):

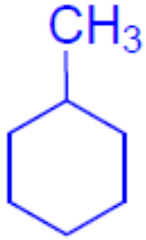
There hydrocarbons contain cyclic "or ring" in all or part of the skeleton. The number of carbon atoms in the ring thus vary They are normally present in the light and the heavy naphtha fractions.



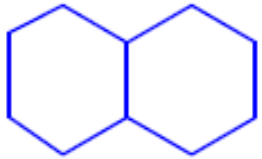
cyclopentane



methylcyclopentane



methylcyclohexane



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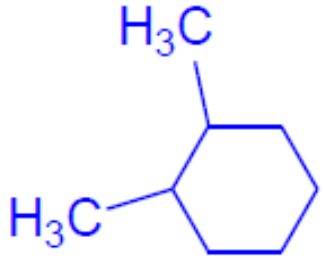


1,2-dimethylcyclohexane

1.3.Aromatic hydrocarbons:

Cyclic and polyunsaturated, aromatics are present in high concentrations in crude oil.

The simplest mononuclear aromatic compound is Benzene (C_6H_6), Toluene (C_7H_8), xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils. Benzene, toluene, and xylenes (BTX) are basic raw material for petrochemical industrial.

2-Non-hydrocarbon Compounds:

2.1. Heteroatomic Organic Compounds:

2.1.1. Sulfur Compounds:

Sulfur is the heteroatom most frequently found in crude oils. Sulfur concentrations can range from lower than 0.05 to more than 10 weight percent; moreover, this content is corrected with the gravity of the crude oil, and therefore, its quality (light or heavy).

Sulfur might present in inorganic forms: element sulfur, hydrogen sulfide, carbonyl sulfide, or positioned within organic molecules as in the following:

Organosulfur compounds may generally be classified as acidic and non-acidic.

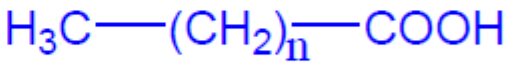
Acidic sulfur compounds are the thiols (mercaptans).

Thiophene, sulfides, and disulfides are examples of non-acidic sulfur compounds found in crude fractions.

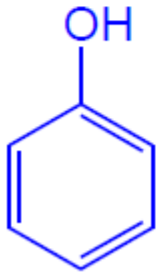
2.1.2. Oxygen Compounds:

Crude oils generally contain less oxygen than sulfur. Even through it is not abundant, oxygen can play a consequential role; in particular, it is responsible for petroleum acidity. Oxygen is found in the following compounds:

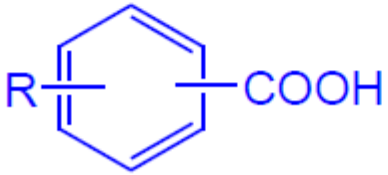
Acidic oxygen compounds:



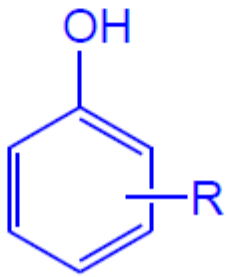
An aliphatic carboxylic acid



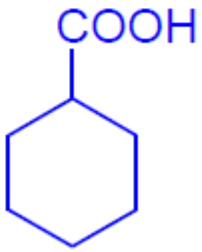
phenol



Aromatic acids



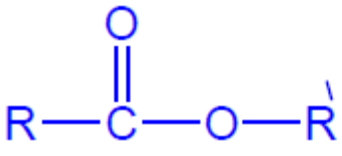
Cresylic acid



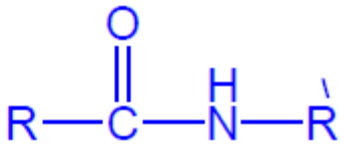
cyclohexanecarboxylic acid

Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds.

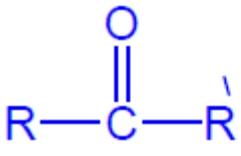
Non-acidic oxygen compounds:



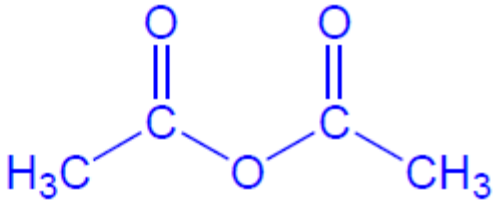
Esters



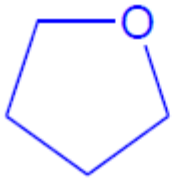
Amides



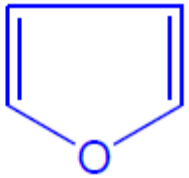
Ketones



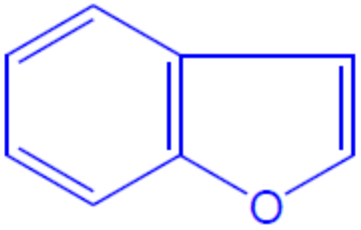
Acetic anhydride



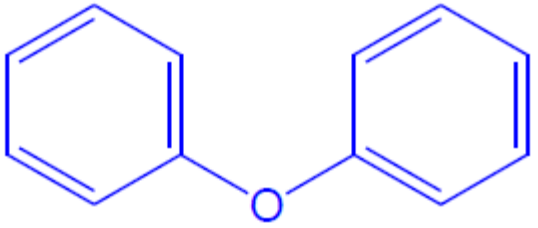
Tetrahydro furane



Furan



Benzofuran

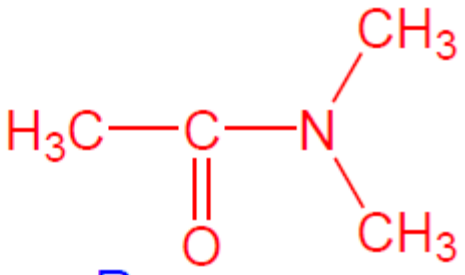


Diphenylether

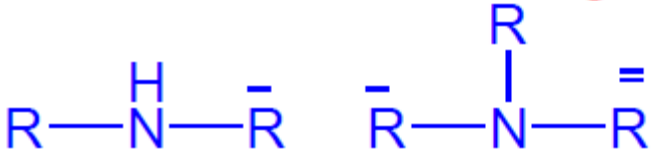
2.1.3. Nitrogen Compounds:

In crude oil, nitrogen is found mostly in fractions boiling over 250°C and is particularly concentrated in resins and asphaltenes. Nitrogen takes the following forms:

- In saturated or aromatic amides:



- As amines: $R—NH_2$



The nitrogen content in most crudes is very low and does not exceed 0.1 wt%. In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt %.

Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin.

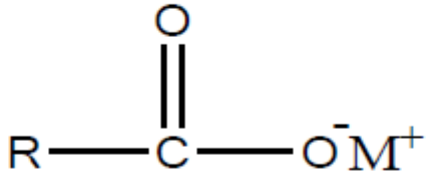
Nitrogen compounds in crudes may generally be classified into basic and non-basic nitrogen compounds . Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure.

2.2.Metallic Compounds:

Many metals occur in crude oils. Such as sodium (Na), calcium (Ca), potassium (K), magnesium (Mg), aluminum (Al), iron (Fe), vanadium (V), and nickel (Ni).

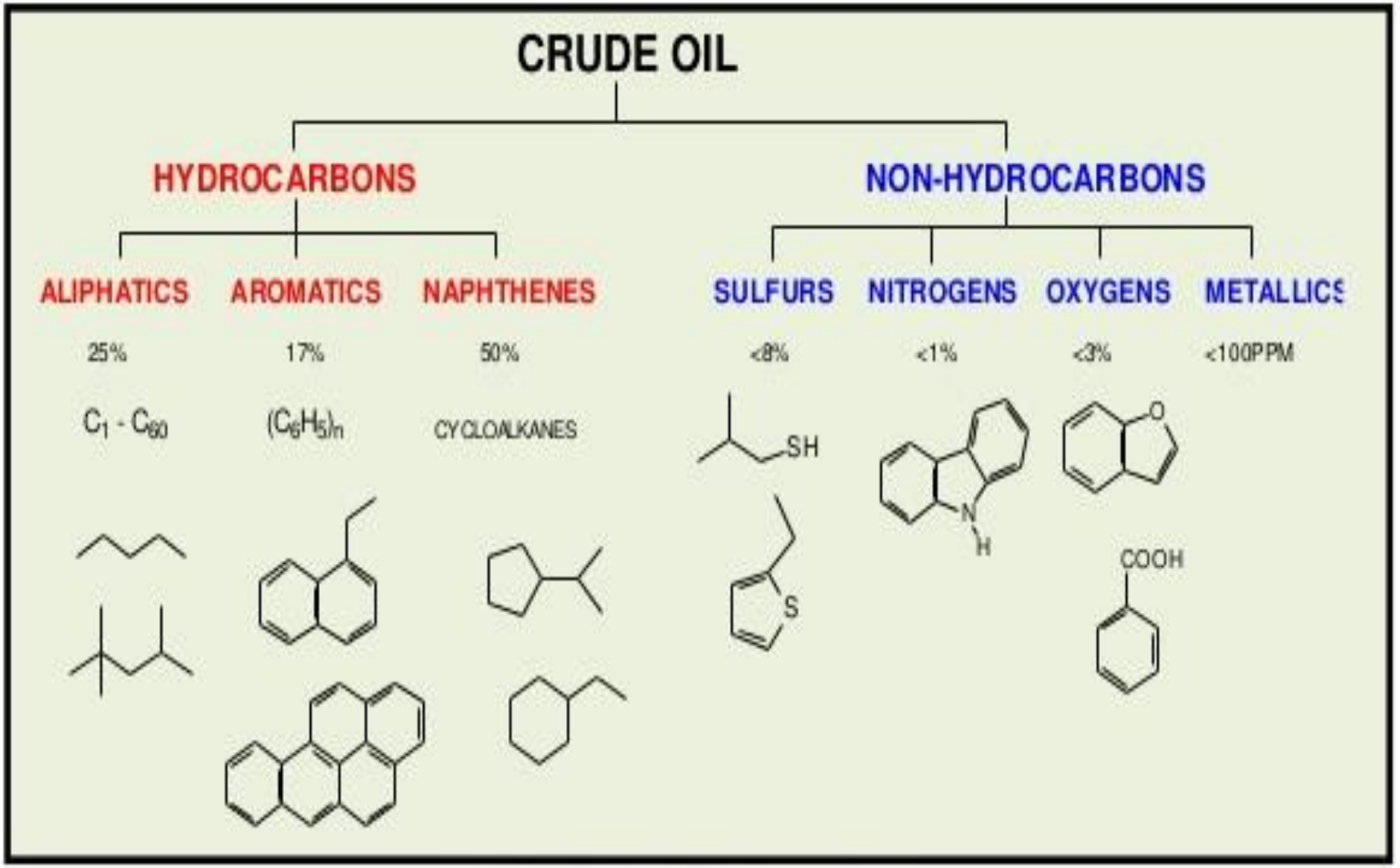
They are present either as inorganic salts, such as sodium and magnesium chlorides (NaCl & MgCl), or in the form of organometallic compounds, such as those of nickel and vanadium (as in porphyrins) .

Calcium and magnesium can form salts or soaps with carboxylic acids.



Where M: Ca, Mg, K, Na

Desalting crude oils is a necessary step to reduce these salts.



Composition of Crude Oil