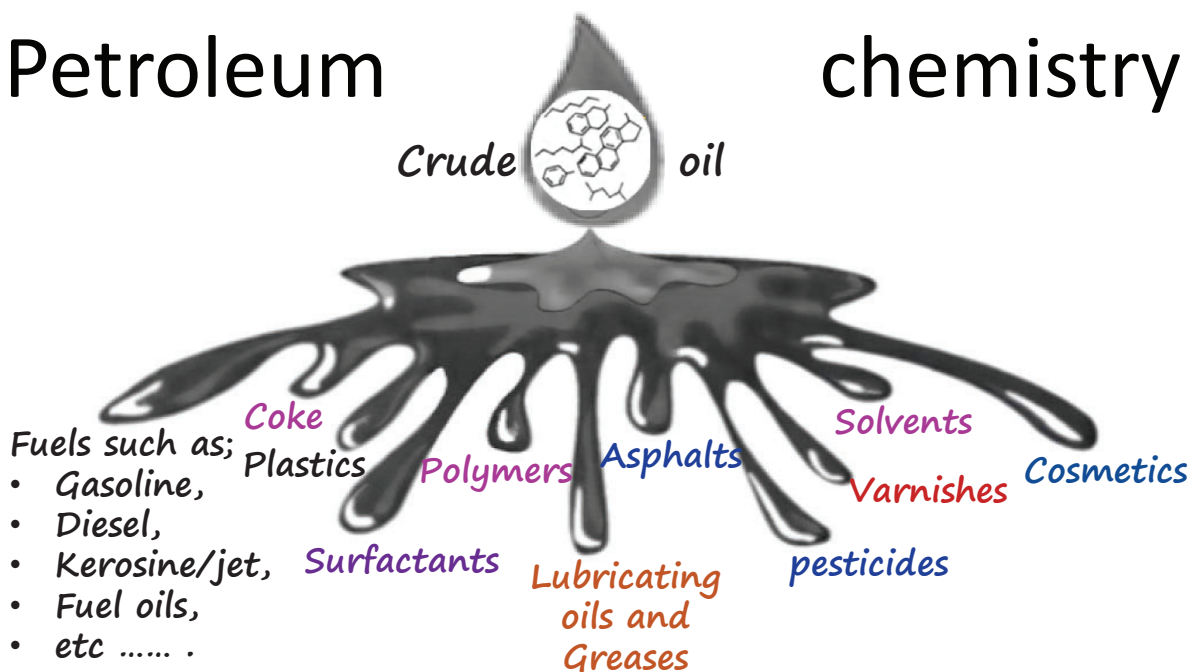


Petroleum

chemistry



Essa I. Ahmed - PhD

essa.ahmed@su.edu.krd

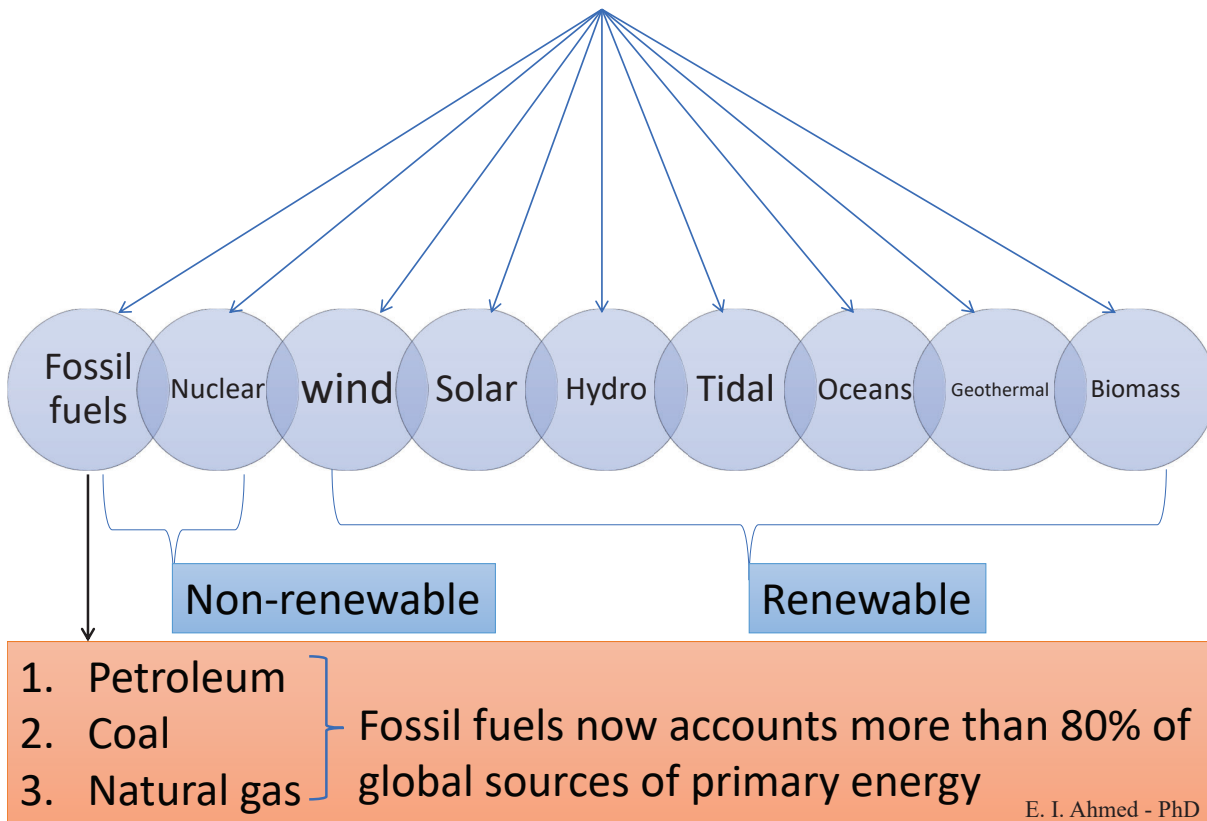
Chemistry Department-College of Education

Salahaddin University- Hawler

Course overview

- Importance of fossil fuels
- Introduction to petroleum
- Chemical constitution of petroleum
- Oil analysis and oil assays
- Introduction to oil refining processes
- Physical processes
- Fractionation (atmospheric and vacuum distillation)
- Extraction (propane deasphalting, solvent extraction and solvent dewaxing)
- Chemical processes
- Thermal processes
- Visebreaking
- Coking
- Catalytic processes
- Fluid catalytic cracking
- Reforming, alkylation, isomerization, polymerization
- Oil products specifications
- Gasoline
- Diesel
- Lubricating oils

Importance of fossil fuels



Introduction to petroleum

- The word *petroleum*, derived from the Latin words *petra* (rock) and *oleum* (oil), means literally rock oil and was first used in 1546 by **Georg Bauer**.
- Petroleum is a complex mixture of hundreds of hydrocarbons that occur in the sedimentary rocks in the form of gases (natural gas), liquids (crude oil), semisolids (bitumen), or solids (wax or asphaltite)
- The lightest hydrocarbon component of petroleum is methane (CH_4), which is the main element of natural gas, and the heaviest components include asphaltenes, with molecular weights higher than 1000 that are found in heavy oils.

Importance of petroleum

- Petroleum is used as a main source of energy for;
 - A. Industry,
 - B. Heating,
 - C. Transportation and
 - D. The raw materials for the petrochemical plants to produce polymers, plastics, and many other products.
- Liquid fuels are normally produced from liquid hydrocarbons, although conversion of non-liquid hydrocarbons such as coal, oil shale, and natural gas to liquid fuels is being investigated,

E. I. Ahmed - PhD

History of oil

- Small surface occurrences of natural gas and oil seeps have been known since ancient time, Sumerians, Assyrians, and Babylonians used crude oil and asphalt more than 5000 years ago. Around 500 BC, Egyptians used asphalt for mummification of their dead rulers and used in weapons as well.
- Some 2000 years ago, Arab scientists developed methods for the distillation of petroleum, and these methods were introduced to Europe by way of Spain.
- Discovery of distillation led to fractionation of petroleum into various products such as naphtha (or naft), and it was used as an illuminant



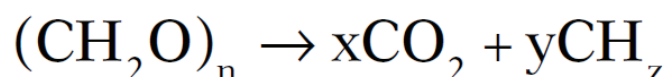
Oil Seep

History of oil

- In 1846, **Abraham Gesner** discovered a process for making a liquid fuel out of coal “kerosine” (or coal oil) and marketed for street lighting in Halifax, Nova Scotia -USA
- At first, the crude oil was refined into kerosene for oil lamps (lighting). However, Gasoline and other products were thrown away because people had no use for them.
- **Henry Ford** started mass producing automobiles in the early 1890’s. Gasoline was the fuel of choice because it provided the greatest amount of energy relative to cost and ease of use.
- Here, the importance of oil was recognized.

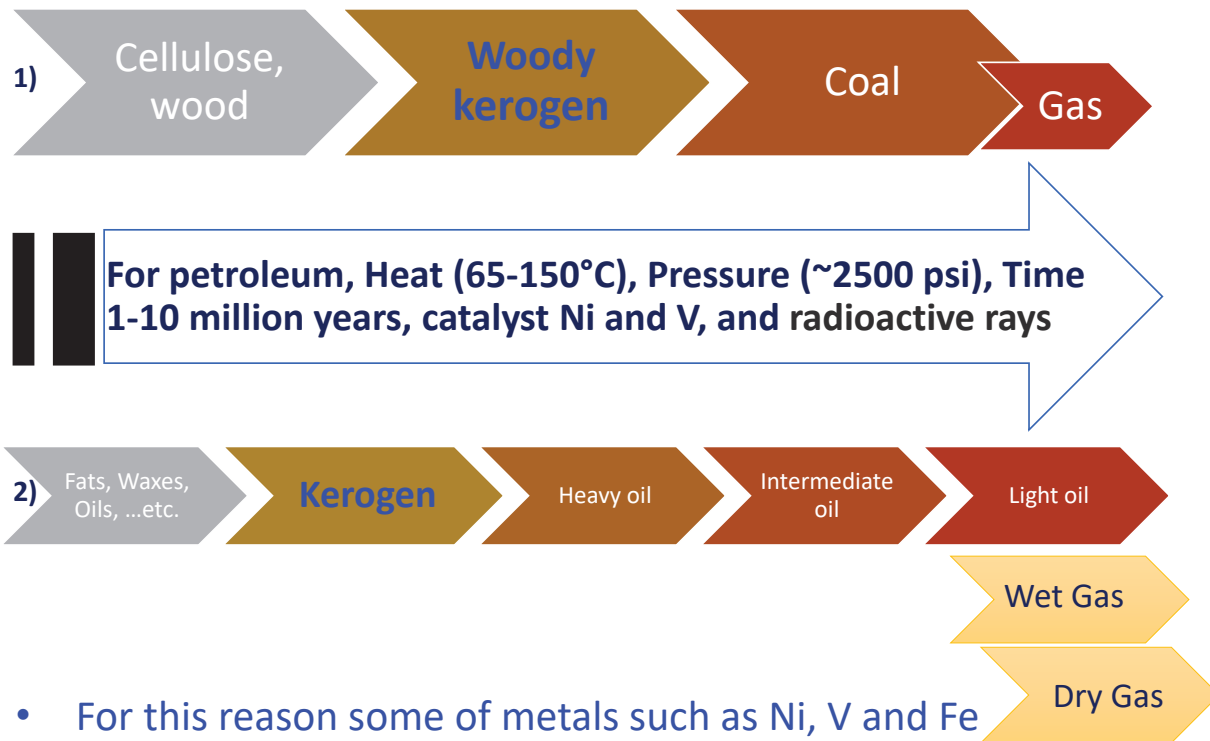
Formation of oil and gas

- **Biogenic theory (next Figures)**, states that petroleum, is formed from remains of **animals and plants (diatoms)** that lived millions of years ago in a **marine environment**. Over millions of years (1-10), the remains of these animals and plants were covered by layers of sand, silt, and rock. **Heat and pressure** from these layers (**2100 to 5300 m**) deep converted the remains into what we now call **crude oil (petroleum)**.



in which **n**, **x**, **y** and **z** are integer numbers and **yCH_z** is the closed formula for the produced **HC** compounds.

Formation of oil and gas



- For this reason some of metals such as Ni, V and Fe are found in small quantities in petroleum fluids,

E. I. Ahmed - PhD

Formation of oil and gas

- Based on **abiotic (abiogenic)** theory two paths are possible for the formation of oil and gas.
- CaCO_3 , an **inorganic compound**, can be converted to CaC_2 , which reacts with **water (H_2O)** to make **acetylene (C_2H_2)**, a hydrocarbon shown below:



- $\text{FeC}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_4 + \text{FeO}_2$
- $\text{Al}_4\text{C}_3 + \text{H}_2\text{O} \longrightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4$
- $\text{R-C} \equiv \text{CH} + \text{H}_2 \xrightarrow{\text{Ni}} \text{R-CH=CH}_2 \xrightarrow[\text{Ni}]{\text{H}_2} \text{RCH}_2\text{-CH}_3$

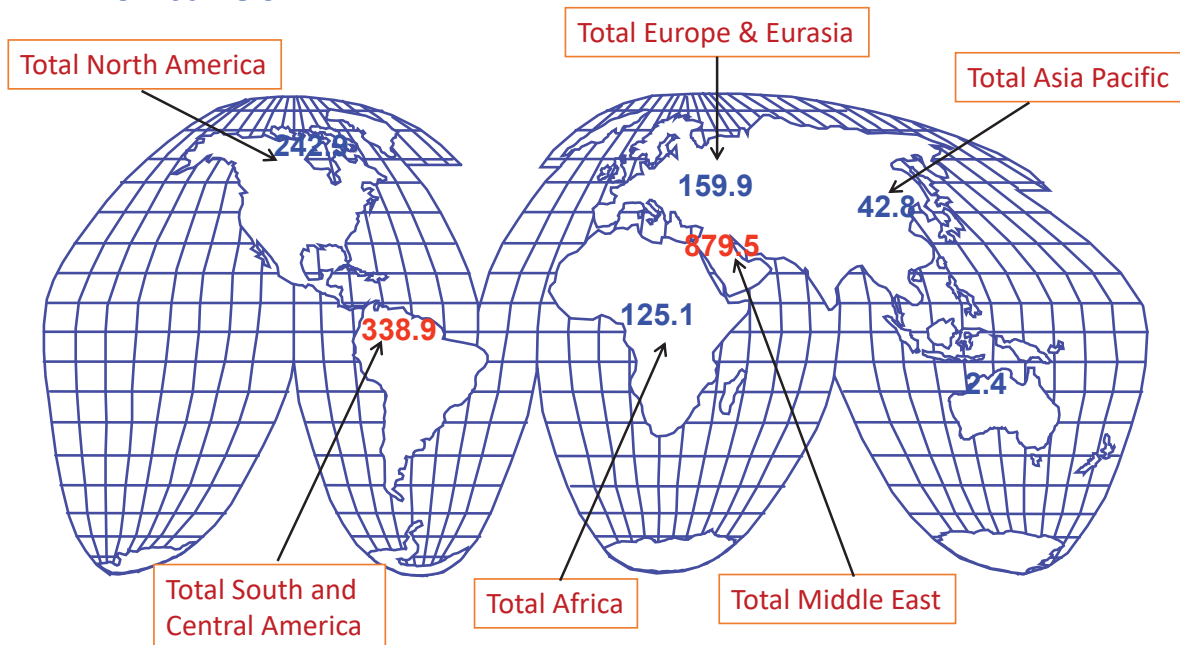
E. I. Ahmed - PhD

Formation of oil and gas

- Either way, an aquatic environment is required for the formation of petroleum and that could be a good reason **why** major oil reservoirs are located in the vicinity (neighborhood) of seas and oceans, **therefore**, major oil fields are found at the seabeds, such those located in Gulf of Mexico or the Persian Gulf in the Middle East (illustrated in next Figure).
- Hydrocarbons produced from organic materials gradually migrate through porous rocks and form a petroleum reservoir when a nonporous or seal rock is found. A series of reservoirs within a common rock form an oil field

Formation of oil and gas

In Billion barrels

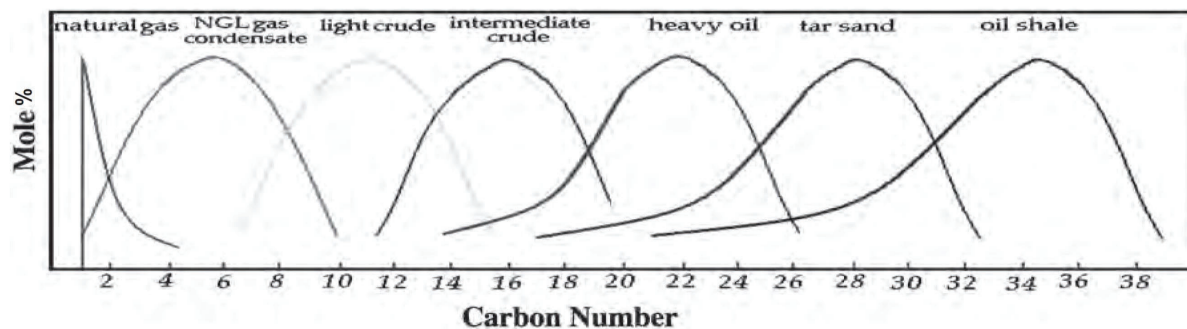
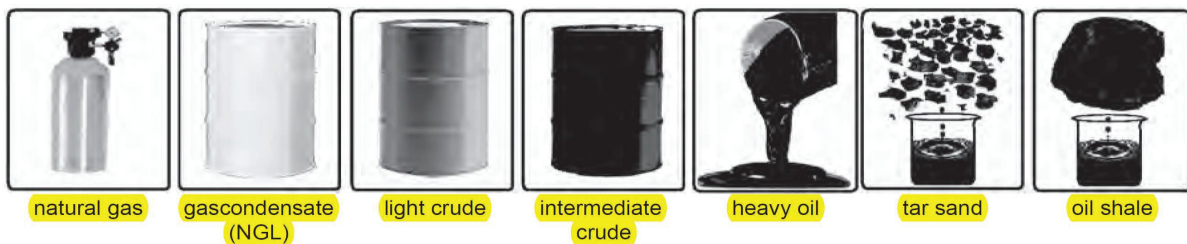


World proven reserves of crude oil at the end of
2023

Types of oil and gas reservoirs

- Hydrocarbons found in different fields and reservoirs vary depending on their **source** and the **maturity of the formation process**, and this leads to the production of different kinds of reservoir fluids as shown below;
- The figure shows various **types of reservoir fluids** starting from **natural gas** to **conventional oil**, **tar sand bitumen** and **oil shale** with approximate **hydrocarbon molecular weight distributions** based on their **carbon numbers**.
- The **heavy fluids** usually **do not flow naturally** (except in hot reservoirs).
- Therefore, it is necessary to apply **artificial heating** or **enhanced recovery technologies** for their extraction, and

Types of oil and gas reservoirs



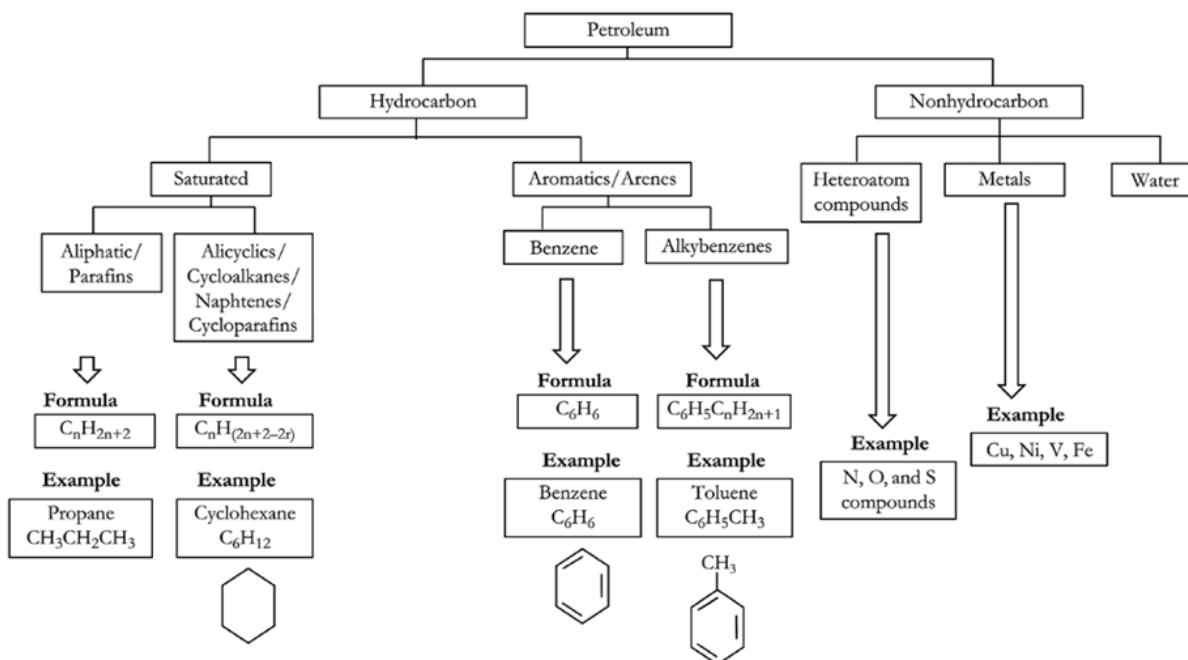
- are considered as **unconventional oils**.
- **Unconventional resources** are hydrocarbons (**crude oil**, **natural gas**, and **condensates**) found in very tight reservoirs.

Chemical composition of petroleum

- Petroleum is a complex mixture of various organic compounds. It consists of different hydrocarbons and nonhydrocarbons (Next Figure).
- Hydrocarbon mixture is highly complex mixture of , paraffinic, naphthenic, and aromatic and sometimes all structures can exist within the same molecule
 - Non-hydrocarbon compounds include
 - S, N, and O containing compounds,
 - Organic metallic (Ni, V, and Fe) containing compounds, and,
 - Inorganic metallic compounds are (Na^+ , Mg^{++} and Ca^{++})

E. I. Ahmed - PhD

Chemical composition of petroleum

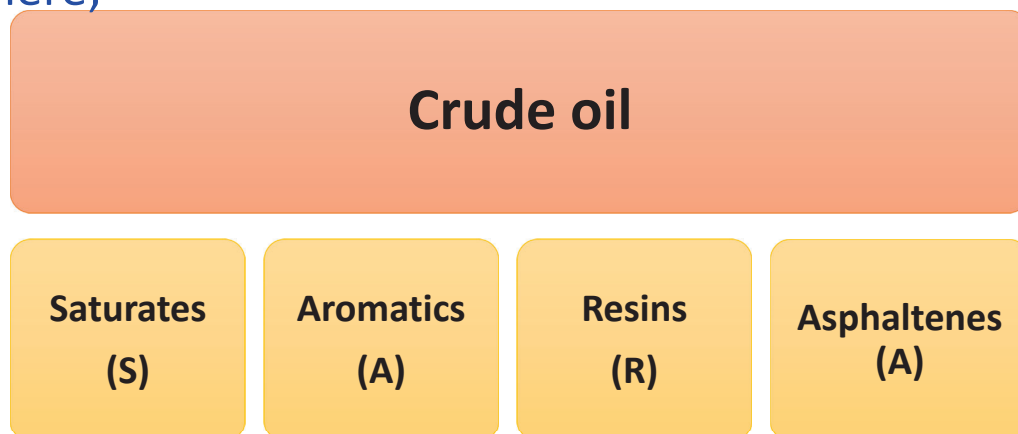


Chemical composition of petroleum

- Hydrocarbons constitute the most important part of any crude oil. Although, their % in different crudes varies significantly (e.g. from 30-40% to 100% in gas condensates), **hydrocarbons comprise up to 70 mass % in all petroleums on the average.**
- Hypothetically, all petroleum hydrocarbons can be subdivided into two main groups:
- 1- **Transformed hydrocarbons** which have lost the structural features of the original biological molecules, and,
- 2- **Biological markers (Biomarkers)** of chemofossils.
- Among the most common biomarkers, **normal and isoprenoid alkanes** and **cyclic isoprenoids**, e.g. **steranes, triterpanes**, are some examples.

Chemical composition of petroleum

- It is generally recognized that crude oils are composed of **four major fractions which are shown here;**



- They differ from one another sufficiently in **solubility** and **adsorptive character** that the separation can be achieved by application of relevant methods

Hydrocarbons (HCs)

- Hydrocarbons constitute the largest group of organic compounds found in petroleum
- There might be as many as several thousand different HCs in crude oil.
- They divided into four main groups:
- Paraffins, Olefins, Naphthens, and Aromatics
- Among these groups, paraffins, olefins, and naphthens are sometimes called aliphatic compounds, as different from aromatic compounds
- Olefins are not usually found in crude oils, but produced in a number of refining processes

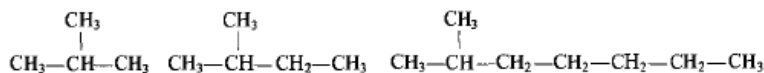
Hydrocarbons (HCs)

A. Paraffinic hydrocarbons;

- Paraffins are divided into two groups; normal and iso-paraffins, some examples are shown below;



n-Heptadecane (C₁₇H₃₆)



isobutane

isopentane (methylbutane)

isooctane (2-methylheptane)



- C₁-C₄ are gases
- C₅H₁₂ -C₁₇H₃₆ are liquids, and,
- C₁₈ H₃₈ or heavier compounds exist as wax-like solids
- Paraffins from C₁ to C₄₀ usually appear in crude oil and represent up to 20 vol. % of crude,