PETROLEUM CHEMISTRY

Classifications of crude petroleum oil

Crudes are commonly classified according to the residue from their distillation, this depending on their relative contents of the three basic hydrocarbons: paraffins, naphthenes and aromatics. About 85 percent of all crude oils fall into the following three classifications:

Asphalt-Based: containing very little paraffin wax and a residue which is primarily asphaltic (predominantly condensed aromatics). Sulfur, oxygen and nitrogen contents are often relatively high. Light and intermediate fractions have high percentages of naphthenes. These crude oils are particularly suitable for making high quality gasoline, machine lubricating oils and asphalt.

Paraffin-Based: containing little or no asphaltic materials, are good sources of paraffin wax, quality motor lube oils, and high grade kerosene. They usually have lower non-hydrocarbon content that do the asphalt base crude.

Mixed-Based: containing considerable amounts of both wax and asphalt. Virtually all products can be obtained, although at lower yields than from the other two classes.

1- Origins of Oil and Gas

1.a Inorganic Theory:

- Inorganic origin source of petroleum was assumed in nineteenth century by:

(A) Berthelot theory (1866):

. This theory regards petroleum origin that carbonic acid or carbonates dissolved in ground water acting on alkali metals present in the earth® interior formed acetylene and other hydrocarbons.

- The formation of acetylene by this reaction was shown to occur, and the production of other hydrocarbons was regarded as possible at high temperature and pressures prevailing at great depths.

(B) Carbide Theory:

· This theory was originally suggested by Mendeleev in the early 1800®, and supported by Mossan, Sabatier and Senderens.

- It regards petroleum as of inorganic origin being formed by the action of steam or water on metallic carbides in the inner portion of earth® crust.
- The carbide theory describes the formation of petroleum by the following steps:

(i) Formation of Carbides: The molten metals in the hot interior of the earth came in contact with coal and carbides were formed, thus:

$$4\ Al + 3\ C \xrightarrow{\Delta} Al_4C_3 \quad \text{(Aluminum carbide)}$$

$$Ca + 2\ C \xrightarrow{\Delta} CaC_2 \quad \text{(Calcium carbide)}$$

(ii) Action of steam on Carbides: Carbides reacted with steam under high pressure and at high temperature forming hydrocarbons.

$$Al_4C_3 + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + \underset{\text{Methane}}{3\ CH_4}$$

$$CaC_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

(iii) Reduction of Unsaturated Hydrocarbons:

- The unsaturated hydrocarbons formed by step (ii) are reduced with hydrogen in the presence of metallic catalyst at high temperature.

The hydrogen needed for reduction is obtained by the action of hot metals with steam.

v) Polymerization: Unsaturated hydrocarbons polymerized in the presence of hot metals forming aromatic hydrocarbons, cycloalkanes, and higher open-chain hydrocarbons.

$$\underset{\text{Acetylene}}{3\ CH\equiv CH} \longrightarrow \underset{\text{benzene}}{C_6H_6}$$

$$\underset{\text{Ethylene}}{2\ CH_2=CH_2} \longrightarrow \underset{\text{2-Butene}}{CH_3CH=CHCH_3}$$

$$\underset{\text{Ethylene}}{3\ CH_2=CH_2} \longrightarrow \underset{\text{Cyclohexane}}{(CH_2)_6}$$

Evidence for the forming of petroleum oil by inorganic theory

1. There is methane and other simple hydrocarbons on other moons, planets, and comets in our solar system and on the meteors that fall to the earth. The hydrocarbons in these objects must have formed without any biotic source

- He believed that petroleum came from deep within the earth, noting how petroleum seemed to be associated with large features of the earth like mountains and valleys rather than the finer scale sedimentary deposits.

- There are many today who believe in this theory, and there is some evidence to back them up.

There is no doubt that the carbide theory explains the formation of petroleum in a rational way but there are serious objections against it and at present this theory commands little consideration.

The main facts which go against it are:

(a) Natural petroleum contains sulphur and nitrogen compounds, chlorophyll, haemen, ect.
The carbide theory fails to explain their presence in petroleum as they are all essentially of organic origin.

(b) Petroleum contains optically active compounds, According to the carbide theory, the natural mode of formation of petroleum is a strict laboratory one and we know that we cannot get optically active substances by ordinary synthetic methods in the laboratory.

(c) The presence of the characteristically organic nitrogen, sulfur and oxygen compounds found in such crude oil have been studied from this stand point, cannot well be explained by any reasonable inorganic theory.

Organic theory

The dominant organic petroleum origin theory directly links petroleum origination to the decomposition of organic matter as:

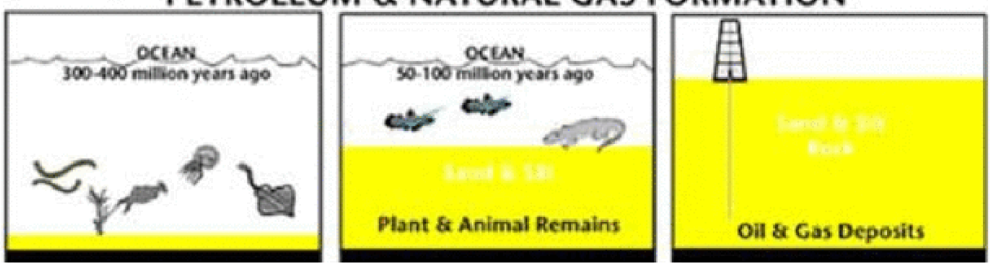
-The oil and gas are formed from remains of prehistoric plants ,animals animals and zooplanktons .

-These remains were settled into seas and accumulated at the ocean floor and buried under several kilometers of sediments.

-Over a few million years, the layers of the organic material were compressed under the weight of the sediments above them.

-The increase in pressure and temperature with the absence of oxygen organic matter into Kerogen. After further burial and heating, the kerogen transformed via cracking into petroleum and natural gas.

PETROLEUM & NATURAL GAS FORMATION

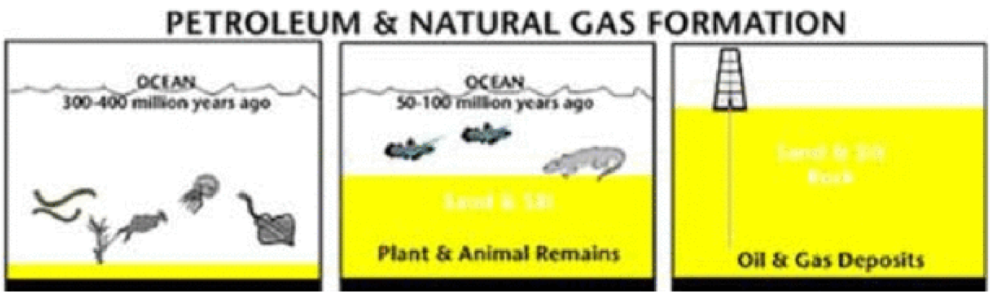


Evidences for organic origin of petroleum

1--Presence of brine (sea water) with petroleum.
2-Petroleum is found only in association with sedimentary rocks. There is no petroleum associated with igneous or metamorphic rocks.
3- The presence of petroleum in the places of the delta of water rivers and bays and near the beaches.
4- Crude oil contains fossils ,shells and remains of ancient living things.
5- The oil contains porphyrin, which indicates the deposition of the petroleum-forming materials under high pressure and temperature.
6- The presence of optically active copmounds in petroleum oil.
7-- The possibility of producing an oil-like liquid when exposing seabed sediments to pressure and temperature

1.b Organic Theory:

- The most popular theory is known as the *Organic Theory*.
- This theory states that oil and gas have biological origins [Engler 1900]. Small sea creatures from the days when the earth was mostly covered in water died and settled to the bottom of the ocean floor.



- Layer upon layer of silt, sand and clay built up on top of them over time.
- Through the process of decay, as well as ever increasing heat and pressure, the former sea creatures were converted to oil and gas.
- Over millions of years, continuous pressure actually compressed those layers of silt and clay into layers of rock. This is known as "reservoir rock".

Diagenesis-catagenesis-metagenesis

The maturation process needs several stages, they are:

- Diagenesis, this stage is the decomposition process occurs and there is a reduction in the oxygen content of organic material with abiotic reactions that produce methane and carbon dioxide kerogen. At this stage the organic material is still immature.

- Catagenesis, burial process continues and the fluid content of hydrocarbons starts out with an initial form of fluid and then the temperature rise resulting gas. At this stage, the percentage of H / C decreases but the O / C is not too reduced.

- Metagenesis, the process continues as a large burial pressure and temperature almost reached metamorphic phase. The end result can be either graphite.

Physical properties of crude oil

Relative density = density of pet. fraction / density of water at the same temperature.

API gravity:

$$^\circ API = \frac{141.5}{Sp.grat\, 60/60^\circ F} - 131.5$$

3. Aniline Point:

The aniline point is a physical characteristic of hydrocarbon compounds, such as oils, and refers to the minimum temperature at which the hydrocarbon and the same amount of the compound aniline ($C_5H_5NH_2$) are perfectly miscible.

The aniline point of a liquid will vary, depending upon the relative concentration of aromatic compounds dissolved in it. Generally, a higher aniline point means a relatively low level of dissolved aromatics. By using reference materials for a pure sample of a given substance and comparing the aniline point of the pure sample to that of the test sample, a chemist can calculate the amount of aromatics in the test sample with a high degree of accuracy.

- Increase by increasing carbon atoms in the paraffinic carbon chain
- Increase by increasing side chains in the paraffinic carbon chain
- Decrease by increasing aromatic content.

4. Flash Point

The **flash point** of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a flash point requires an ignition source

5. Fire Point

The **fire point** of a fuel is the temperature at which the vapour produced by that given fuel will continue to burn for at least 5 seconds after ignition by an open flame. At the flash point, a lower temperature, a substance will ignite briefly, but vapor might not be produced at a rate to sustain the fire.

5- Viscosity :-

Kinematic viscosity: a measure of the time for a fixed volume of liquid to flow by gravity through a capillary. The cgs (centimeter-gram-second) unit of kinematic viscosity is the **stoke** which has the dimensions centimeters-squared per second. In the petroleum industry kinematic viscosity is usually expressed in centistokes, cSt, so that 1 St = 100 cSt.

$$\text{Kinematic viscosity, cSt} = C \cdot t$$

where:

C = calibration constant of the viscometer, cSt/s, and
t = flow time, s.

Dynamic viscosity:- (sometimes called absolute viscosity) is numerically the product of kinematic viscosity and the density of the liquid, both at the same temperature. The cgs unit of dynamic viscosity is the **poise**, P, which has the dimensions grams per centimeter per second. It is the force required to move a unit plane surface over another plane surface at unit velocity when surfaces are separated by a layer of fluid of unit thickness.

$$\text{Dynamic viscosity, cP} = \rho \cdot \nu$$

where:

ρ = density, g/cm³ (Note 6) at same temperature as kinematic viscosity, and
ν = kinematic viscosity, cSt.

6- Pour point :-

The **pour point** of a liquid is the temperature at which it becomes semi solid and loses its flow characteristics. In crude oil a high pour point is generally associated with a high paraffin content, typically found in crude deriving from a larger proportion of plant material.

7- Freezing Point:

The **melting point** of a solid is the temperature at which it changes state from solid to liquid at atmospheric pressure. At the melting point the solid and liquid phase exist in equilibrium. The melting point of a substance depends on pressure and is usually specified at standard pressure. When considered as the temperature of the reverse change from liquid to solid, it is referred to as the **freezing point** or **crystallization point**.

Diesel Index

The Diesel Index indicates the ignition quality of the fuel. It is found to correlate, approximately, to the cetane number of commercial fuels. It is obtained by the following equation

$$Diesel\ Index = \frac{aniline\ point\ (^{\circ}F)\ x\ Degrees\ API\ gravity\ (60^{\circ}F)}{100}$$

high-quality fuel has a high index number.

Aniline point used to determine cetane number and Disel index.

Cetane no.=0.72*D.I + 10

REFRACTIVE INDEX :

The refractive index is the ratio of the velocity of light in a vacuum to the velocity of light in the substance. The measurement of the refractive index is very simple, requires small quantities of material, and, consequently, has found wide use in the characterization of hydrocarbons and petroleum samples.

The refractive and specific dispersion, as well as the molecular and specific refraction, have all been advocated for use in the characterization of petroleum and petroleum products. The refractive dispersion of a substance is defined as the difference between its refractive indices at two specified wavelengths of light. Two lines, commonly used to calculate dispersions are, the C (6563 Å, red) and F (4861 Å, blue) lines of the hydrogen spectrum. The specific dispersion is the refractive dispersion divided by the density at the same temperature:
Specific dispersion = $n_F - n_C/d$

This equation is of particular significance in petroleum chemistry because all the saturated hydrocarbons, naphthene and paraffin, have nearly the same value irrespective of molecular weight, whereas aromatics are much higher and unsaturated aliphatic hydrocarbons are intermediate.

Cetane number

Cetane number or CN is an indicator of the combustion speed of diesel fuel. It is an inverse of the similar octane rating for gasoline (petrol). The CN is an important factor in determining the quality of diesel fuel. Cetane number is an inverse function of a fuel's ignition delay, the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel.

Cetane number is a percentage of pure Cetane in a mixture of cetane and alpha methyl naphthalene the latter matches the ignition quality of kerosene sample

Octane number (Octane rating)

Measure of the ignition quality of gas (gasoline or petrol). Higher this number, the less susceptible is the gas to **@knocking@** (explosion caused by its premature burning in the combustion chamber) when burnt in a standard (spark-ignition internal combustion) engine.

Octane number denotes the percentage (by volume) of iso-octane (a type of octane) in a combustible mixture (containing iso-octane and normal-heptane) whose @anti-knocking@characteristics match those of the gas being tested.

. Branched-chain paraffinic hydrocarbons have high octane number than straight-chain paraffinic hydrocarbons. The straight-chain paraffins are converted to their branched-chain paraffins to increase the octane number (isomerization process).

. Aromatic and alkyl aryl hydrocarbons have very high octane number, addition of aromatic compounds (toluene, xylene, etc.) to gasoline to raise its octane rating is limited by environmental regulations ±health effects due to high toxicity.

. Olefinic hydrocarbons have high octane number

. Sulfur compounds decrease the octane number.