Origin of Petroleum

- Inorganic or Organic?
- Debated for many years
- Now most scientist agree on ORGANIC origin
- Oil forms from the decay and transformation of dead organisms buried in sedimentary rocks

Generalities of the origin of hydrocarbons

Two possible sources: Inorganic and organic

- **Inorganic**- Hydrocarbons form from reduction of primordial carbon or oxidized forms at high temperatures in the earth
- **Organic-** accumulation of hydrocarbons produced directly by living organisms, as well as the thermal alteration of biologically formed organic matter.
  - It is generally recognized that most hydrocarbons are produced by the organic method. A few hydrocarbons in the crust may be from inorganic sources, but the majority of them are from organic.

The Inorganic Theory

- The first to advance a general inorganic theory was Berthelot, who, proceeding upon the hypothesis of Daubree that the interior of the earth contains free alkali metals, ascertained, by experiment, that when carbonic acid or an earthy carbonate comes in contact with the alkali metals at a high temperature, acetylides are formed.
- These acetylides yield hydrocarbons when acted on by water under suitable conditions

The Inorganic Theory

- He therefore expressed the view, in 1866, that petroleum may have been produced by filtration of water containing carbonic acid gas into the interior of the earth, where it would come in contact with alkali metals at an elevated temperature, under great pressure, and produce both liquid and gaseous hydrocarbons.

The Carbide Theory

- Proposed by Mandeleef in 1886
- His assumption is that deep within the Earth there are compounds called metal carbides, which react with water in the form of hydrothermal solutions.
- In the most basic case, iron carbide plus water reacts to form iron oxide (better known as "rust") plus acetylene, the well-known industrial gas.

The Carbide Theory

- According to the Carbide Theory, The molten metals in the interior of the earth reacted with coal deposits under pressure and high temperatures to form carbides

  $Ca + 2C \rightarrow CaC_2$ (Calcium Carbide)

  $4Al + 3C \rightarrow Al_4C_3$ (Aluminum Carbide)

  $Mg + 2C \rightarrow MgC_2$ (Magnesium Carbide)

The Carbide Theory

- Subsequently these carbides react with steam or water under high pressure and temperature to give a mixture of hydrocarbons

  $CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$ (Acetylene)

  $Al_4C_3 + H_2O \rightarrow 4Al(OH)_3 + CH_4$ (Methane)

The Carbide Theory

- In the presence of these metal catalysts and under conditions of high temperature and pressure, the unsaturated hydrocarbons undergo the following types of reactions
  - Hydrogenation
  - Polymerization
  - Isomerization
  - Alkylation

Carbide Theory

- Hydrogenation

  $C_2H_2 + H_2 \rightarrow C_2H_4$

  $C_2H_4 + H_2 \rightarrow C_2H_6$

  $CH_3\text{-}CH{=}CH\text{-}CH_3 + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ (Butane)

  1-Hexene or 2-Hexene $\rightarrow C_6H_{14}$ (Hexane)
- Polymerization

  $2C_2H_4 \rightarrow CH_3\text{-}CH{=}CH\text{-}CH_3$ (2-butene)

  $3C_2H_4 \rightarrow C_6H_{12}$ (Cyclohexane)

  $3C_2H_4 \rightarrow C_6H_6$ (Benzene)
- Isomerization

  $CH_3\text{-}CH{=}CH\text{-}CH_3 + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH{=}CH_2$ (1-Butene)
- Alkylation

  $CH_3\text{-}CH_2\text{-}CH{=}CH_2 + C_2H_4 \rightarrow$ 1-Hexene + 2-Hexene

Carbide Theory

- The Carbide theory fails to account for the following
  - Natural petroleum contains
    - Compounds of N and S
    - Compounds like chlorophyll, haemin etc
    - Optically active compounds
    - Sea water and brine

Engler's Theory

- Engler suggested that petroleum is formed by the decay and decomposition of animals under high pressure and temperature
- These animals are preferably of sea origin

Engler's Theory

His arguments

- If a volcano erupts by the sea side then poisonous gases like sulphur dioxide given out by the volcano may dissolve in sea water
- Consequently fishes and other marine animals may die of suffocation
- In due course of time this results in accumulation of dead animals
- If somehow this zone gets covered by the earth's hot crust, high temperature and pressure converts the remains into petroleum.

Engler's Theory

- Engler supported his theory by the destructive decomposition of fish oil and other animal fats under high pressure and temperature.
- This yielded a product similar to natural petroleum
- This contained compounds of N and S
- This contained optically active compounds

Engler's Theory

Engler's theory is supported by the following facts

- Presence of Brine or sea water with petroleum
- Presence of optically active compounds
- Presence of N and S containing compounds
- Presence of Fossils

Engler's Theory

Engler's theory fails to account for the following

- Presence of Chlorophyll
  - He talks only about animals
- Presence of coal deposits found near the oil fields
- High resin content of certain oils

The Organic Theory Modern Theory

- Over geological time the organic matter mixed with mud, and was buried under heavy layers of sediment resulting in high levels of heat and pressure (known as diagenesis). This caused the organic matter to chemically change, first into a waxy material known as **kerogen** which is found in various oil shales around the world, and then with more heat into liquid and gaseous hydrocarbons in a process known as **catagenesis**.

The Organic Theory Modern Theory

- The organic theory holds that the first stage of the genesis of petroleum involves plankton (single-celled organisms that float on the oceans).
- These die and gradually accumulate on the ocean floor.
- Other sediments start accumulating too, and after a few million years the plankton are buried under several km of sediment.
- The plankton, which have remained unoxidised, under the increased values of pressure and temperature, are now transformed into kerogen.

The Organic Theory Modern Theory

- Under favorable conditions of time and temperature this kerogen, after further burial and heating, is transformed, via cracking, into petroleum and natural gas.
- These then migrate towards the surface and end up either reaching it (and drying up to yield bitumen or tar) or being arrested on the way in traps (where, millions of years later, drillers of the present industrial age make their big strikes)

The Organic Theory Modern Theory

- Geologists view crude oil and natural gas as the product of compression and heating of ancient organic materials (i.e. kerogen) over geological time.
- Formation of petroleum occurs from hydrocarbon pyrolysis, in a variety of mostly endothermic reactions at high temperature and/or pressure.
- Today's oil formed from the preserved remains of prehistoric zooplankton and algae, which had settled to a sea or lake bottom in large quantities under anoxic conditions (the remains of prehistoric terrestrial plants, on the other hand, tended to form coal).

The Organic Theory Modern Theory

- Since it is known that hydrocarbons can be produced by photosynthesis, it is natural to expect petroleum to be of an organic origin.
- Molecules thought to be of biological origin, e.g.: porphyrins, isoprenoids, hopanoids, etc. were found in petroleum, thereby providing support for the organic theory.
- The organic carbon in plants is depleted in carbon-13 due to the process of photosynthesis. In dead organic material the C-13 is further depleted due to radioactive decay. Since it was found that most petroleum and natural gas showed the same depletion, it was viewed as a strong proof in favour of an organic origin.

The Organic Theory Modern Theory

- Sediments are the most important host rocks yielding petroleum, i.e. the oil produced from oil wells is generally obtained from a porous sandstone deep below. Often sediments are associated with biological material that could have acted as a source of the petroleum.
- The existence of large quantities of oil shale from which a hydrocarbon mix similar to petroleum could be distilled was seen as a support in favour of an organic origin. This followed easily, since the oil shale was taken to be the kerogen source rock which, on sufficient burial, purportedly yielded petroleum.

Origin of Petroleum

- The debate about cooking up hydrocarbons keeps getting hotter
- Some scientists insist that all petroleum comes from abiogenic processes, with hydrocarbon development occurring in the Earth's mantle.
- Most geochemists and petroleum geologists remain convinced that crude oil and natural gas have organic origins.
- Hence a duplex theory combining features of all the theories may be the final victor. This would perhaps involve the enrichment of existing organic hydrocarbon deposits through non organic hydrocarbons.