Sources of hydrocarbon.

Mineral oil or crude oil, petroleum [Petra → rock; oleum → oil] is the dark color oily liquid [do with offensive odour found at various depths in many regions below the surface of the earth. It is generally found under the rocks of earth's crust and often floats over salted water.

(1) **Composition**

(i) **Alkanes:** found 30 to 70% contain up to 40 carbon atom. Alkanes are mostly straight chain but some are branched chain isomers.

(ii) **Cycloalkanes**: Found 16 to 64% cycloalkanes present in petroleum are; cyclohexane, methyl cyclopentane etc. cycloalkanes rich oil is called asphattic oil.

(iii) **Aromatic hydrocarbon:** found 8 to 15% compound present in petroleum are; Benzene, Toluene, Xylene, Naphthalene etc.

(iv) **Sulphur, nitrogen and oxygen compound**: Sulphur compound present in the extent of 6% and include mercaptans [R-SH] and sulphides [R-S-R]. The unpleasant smell of petroleum is due to sulphur compounds. Nitrogen compounds are alkyl pyridines, quinolines and pyrroles. Oxygen compounds present in petroleum are. Alcohols, Phenols and resins. Compounds like chlorophyll, haemin are also present in it.

(v) **Natural gas**: It is a mixture of Methane (80%), Ethane (13%), Propane (3%), Butane (1%), Vapors of low boiling pentanes and hexanes (0.5%) and Nitrogen (1.3%). L.P.G. Contain butanes and pentanes and used as cooking gas. It is highly inflammable. This contain, methane, nitrogen and ethane.

(vi) **C.N.G.:** The natural gas compressed at very high pressure is called compressed natural gas (CNG). Natural gas has octane rating of 130 it consists, mainly of methane and may contain, small amount of ethane and propane.

(2) Theories of origin of petroleum: Theories must explain the following characteristics associated with petroleum,

Its association with brine (sodium chloride solution). The presence of nitrogen and sulphur compounds in it. The presence of chlorophyll and haemin in it. Its optically active nature. Three important theories are as follows.

(i) **Mendeleeff's carbide theory or inorganic theory**

(a) Molten metals in hot earth's crust combine with coal deposits and formed carbides.

(b) Carbides reacted with steam or water under high temperature and pressure to form mixture of saturated and unsaturated hydrocarbons.

(c) The unsaturated hydrocarbon in presence of metal catalyst, high pressure and high temperature, undergoes reactions such as hydrogenation, isomerization and polymerization to form number of hydrocarbons.

Reactions: $Ca + 2C \rightarrow CaC_2$ (Calcium carbide); $Mg + 2C \rightarrow MgC_2$ (Magnesium carbide)

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

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$ (Acetylene)

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$ (Methane); $C_2H_2 \xrightarrow{H_2} C_2H_4 \xrightarrow{H_2} \underset{\text{(Ethane)}}{C_2H_6}$

$3[CH \equiv CH] \xrightarrow{\text{Polymerisation}} \underset{\text{(Benzene)}}{C_6H_6}$;

$CH_3 - CH = CH - CH_3 \xrightarrow{\text{Isomerisation}} \underset{\text{(1-Butene)}}{CH_3 - CH_2 - CH = CH_2}$

Theory fails to account for, The presence of nitrogen and sulphur compounds. The presence of chlorophyll and haemin derivatives. The presence of optically active compounds.

(ii) **Engler's theory or organic theory:** Theory is supported by the following facts,

(a) The presence of brine with petroleum,

(b) The presence of optically active compounds,

(c) The presence of nitrogen and sulphur compounds

(d) The presence of fossils in the petroleum area.

The theory was further supported by the fact that when destructive distillation of fish oil and other animals fats under high temperature and pressure was carried out, a petroleum like liquid was obtained.

Theory fails to account for, The presence of chlorophyll in the petroleum. The presence of coal deposits found near the oil fields. The presence of resins in the oil.

(iii) **Modern theory:** This theory explain nearly all the facts about petroleum.

(a) The presence of chlorophyll and haemin in petroleum.

(b) The presence of coal deposits near oil fields suggesting its vegetable origin.

(c) The presence of nitrogen and sulphur compounds along with optically active compounds in petroleum.

(d) The presence of resins also suggests that oil must have been formed from vegetable substances.

(e) The presence of helium gas in natural gas suggests that radioactive substances must have helped in the decomposition of organic matter.

(3) **Mining of petroleum:** Petroleum deposits occurs at varying depth at different places ranging from 500 to 15000 feet. This is brought to the surface by artificial drilling.

(4) **Petroleum refining:** Separation of useful fractions by fractional distillation is called petroleum refining.

Fraction	Boiling range (°C)	Approximate composition	Uses
Uncondensed gases	Up to room temperature	$C_1 - C_4$	Fuel gases: refrigerants; productionof carbon black, hydrogen; synthesis of organic chemicals.
Crude naphtha on refractionation yields,	$30 - 150^o$	$C_5 - C_{10}$	
(i) Petroleum ether	$30 - 70^o$	$C_5 - C_6$	Solvent
(ii) Petrol or gasoline	$70 - 120^o$	$C_6 - C_8$	Motor fuel; dry-cleaning; petrol gas.
(iii) Benzene derivatives	$120 - 150^o$	$C_8 - C_{10}$	Solvent; dry-cleaning
Kerosene oil	$150 - 250^o$	$C_{11} - C_{16}$	Fuel; illuminant; oil gas
Heavy oil	$250 - 400^o$	$C_{15} - C_{18}$	As fuel for diesel engines; converted to gasoline by cracking.
Refractionation gives,			
(i) Gas oil			
(ii) Fuel oil			
(iii) Diesel oil			
Residual oil on fractionation by vacuum distillation gives,	Above 400^o	$C_{17} - C_{40}$	
(i) Lubricating oil		$C_{17} - C_{20}$	Lubrication
(ii) Paraffin wax		$C_{20} - C_{30}$	Candles; boot polish; wax paper; etc.
(iii) Vaseline		$C_{20} - C_{30}$	Toilets; ointments; lubrication.
(iv) Pitch		$C_{30} - C_{40}$	Paints, road surfacing
Petroleum coke (on redistilling tar)			As fuel.

(5) Purification

(i) **Treatment with concentrated sulphuric acid:** The gasoline or kerosene oil fraction is shaken with sulphuric acid to remove aromatic compounds like thiophene and other sulphur compound with impart offensive odour to gasoline and kerosene and also make them corrosive.

(ii) **Doctor sweetening process:** $\underset{\text{Mercaptan}}{2RSH} + Na_2PbO_2 + S \rightarrow \underset{\text{Disulphide s}}{RSSR} + PbS + 2NaOH$

(iii) **Treatment with adsorbents**: Various fractions are passed over adsorbents like alumina, silica or clay etc., when the undesirable compounds get adsorbed.

(6) **Artificial method for manufacture of Petrol or gasoline**

(i) Cracking, (ii) Synthesis

(i) **Cracking:** It is a process in which high boiling fractions consisting of higher hydrocarbons are heated strongly to decompose them into lower hydrocarbons with low boiling pts. Cracking is carried out in two different ways.

(a) Liquid phase cracking: In this process, the heavy oil or residual oil is cracked at a high temperature (475 – 530^{o}C) under high pressure (7 to 70 atmospheric pressure). The high pressure keeps the reaction product in liquid state. The conversion is approximately 70% and the resulting petrol has the octane number in the range 65 to 70.

The cracking can be done in presence of some catalysts like silica, zinc oxide, titanium oxide, ferric oxide and alumina. The yields of petrol are generally higher when catalyst is used.

(b) Vapor phase cracking: In this process, kerosene oil or gas oil is cracked in vapor phase. The temperature is kept 600 – 800^{o}C and the pressure is about 3.5 to 10.5 atmospheres. The cracking is facilitated by use of a suitable catalyst. The yields are about 70%.

(ii) **Synthesis:** Two methods are applicable for synthesis.

(a) Bergius process: This method was invented by Bergius in Germany during First World War.

Coal $+ H_2 \xrightarrow[\substack{450-500^o C \\ 250 \text{ atm}}]{Fe_2O_3}$ Mix. Of hydrocarbons or crude oil

(b) Fischer- tropsch process: The overall yield of this method is slightly higher than Bergius process.

$$H_2O + C \xrightarrow{1200^o C} \underbrace{CO + H_2}_{\text{Water gas}}$$

$xCO + yH_2 \longrightarrow$ Mix. Of hydrocarbon $+ H_2O$.

The best catalyst for this process is a mixture of cobalt (100 parts), thoria, (5 parts), magnesia (8 parts) and kieselguhr (200 parts).