Ch – Petroleum :

Petroleum (Mineral oil since it occurs beneath the earth)
derived from | Latin words

- Petra (rock)
- oleum (oil)

* Main source for fuels like petrol or gasoline, diesel, Kerosene, spirit, etc.
* Also source for petrochemicals like alkane, alkene which are converted to ethanol, acetic acid, styrene which are important industrially.

→ **Composition of Petroleum :**

C = 80 to 87 %.
H = 11.1 to 15 %.
S = 0.1 to 3.5 %.
N = 0.4 to 9 %.
O = 0.1 to 0.9 %.

→ **Constituents of petroleum :**

① Hydrocarbons → Normal alkanes, branched alkanes, alkenes, cycloalkanes, cycloalkenes, aromatic hydrocarbon, etc.

(ii) Sulphur compounds :- S_8 or, H_2S, thiophene, thiol, etc.

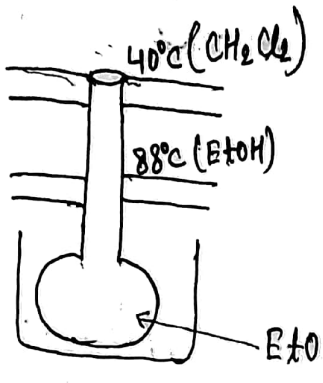
(iii) Nitrogen compounds :- Pyridine, Pyrrole, indole, quinoline, etc.

(iv) Oxygen compounds :- $C_4 - C_9$ carboxylic acids

(v) Organometallic compounds :- compounds of Fe, Ni, V, etc.

→ **Refining of crude oil :-** In order to refine crude oil, first all the impurities like S, N, O based compounds must to be removed from the crude oil and then the crude oil is purified. This process is known as refining of crude oil and plant setup for this purpose is called oil refinery.

Crude oil
↓ removal of impurities like S, N, O
Crude oil having mixture of hydrocarbons
↓ seperation of different fractions by a process
Known as fractional distillation.



Boiling point
CH_2Cl_2 → 40°c
EtOH → 88°c

→ Steps for purifying crude oil:

Step-I:
At first, crude oil is allowed to pass through two highly charged electrodes so that water and other polar compounds removed from the crude oil. Then, crude oil is allowed to react with copper oxides resulting in the formation solid CuS which can be easily seperated from the crude oil by filteration.

Step-II:
A mixture of hydrocarbons having different boiling point are seperated by fractional distillation. In order to do that, crude oil is heated at about 400°c so that all the volatile components gets evaporated. As the vapours go up, condensation takes place at different heights of fractionating column, used for fractional distillation. Heavier boiling mixture condenses first while lower boiling fractions condenses later.

Fraction Name	Boiling point	Constituent	Uses
① Refining gas	<30°C	C_1 to C_4	LPG fuel
② Petroleum ether	30°-70°C	C_5 to C_7	Used as solvate in Laboratory.
③ Gasoline or Petrol	40°-120°C	C_5 to C_8	Fuel for petrol engine.
④ Naptha or Spirit	120°-180°C	C_9 to C_{10}	Used for paint, varnishing, dry cleaning.
⑤ Kerosene	180°-250°C	C_{10}-C_{16}	Domestic fuel, Jet engine fuel
⑥ Diesel	250°-320°C	C_{15}-C_{18}	Fuel in diesel engine.
⑦ Heavy oil	320°-400°C	C_{19}-C_{30}	Provides gasoline on cracking.

* Internal Combustion (IC) Engines :-

Mixture of fuel + air
↓ Ignited
↓ by electric spark (Petrol engine)
↓ by compressing air (Diesel engine)

. 4-stroke IC Engines : (Petrol engine)

(i) Intake stroke :- A mixture of fuel vapour and air is drawn into the cylinder (Sucction stroke).

(ii) Compression stroke :- The Piston compresses the mixture.

(iii) Power stroke :- The mixture is ignited by an electric spark. Gases evolved under high pressure force the piston out, thus providing the power stroke.

(iv) Exhaust stroke :- The system ascends and expels the exhaust gases.

NOTE :- Oil must be completely evaporate before drawn into the cylinder otherwise there will be incomplete combustion, leading to a starting problem. It occurs mainly in winter.

* Knocking :- In 4-stroke IC engines, if the compression stroke raises the temperature higher than the self ignition temperature, it results in self combustion even before ignition step, leading to a rattling sound known as Knocking.

. Consequences of Knocking :-
1) Mechanical damage of the cylinder due to overheating of cylindrical walls.

. Reason for Knocking :-
i) Engine design.
ii) Running condition.
iii) Chemical structure of fuel.

* Free radical chain reaction leading to cracking and oxidation of Hydrocarbon

- Knocking tendency :-

alkane > substituted alkane > cycloalkane > alkene > poly-substituted alkene > aromatics.

→ For straight chain alkane, Knocking increases with increasing molecular weight.

n-hexane > n-pentane > n-butane.

→ The efficiency of petrol towards Knocking is expressed by octane rating.

Fuel	octane no.	Characteristics
n-heptane	0	Knocks severly
iso-octane	100	Knocks very little.

→ Octane Number → Percentage of iso-octane in a mixture of n-heptane and iso-octane which has the same Knocking characteristics as the gasoline sample.

→ Additives such as ~~Tetraethyl Lead~~

TEL → Tetra ethyl Lead (Et_4Pb)

Diethyl tellwride (Et_2Te)

Along with Tetraethyl Lead, Ethylene bromide is recommended.

TEL

↓ combustion

Pb, PbO (acts as free radical scavanger)

↓

quench the propagation step

by forming volatile $PbBr_2$

* Unleaded Petrol → Whose octane number is increased without adding Pb compounds.

* **Diesel Engine:** Only air is drawn into the cylinder and compressed to such an extent that temp. reaches nearly 500°C. Towards the end of the compression stroke, diesel fuel is injected into the cylinder. The fuel absorbs the heat and ignites as it reaches its ignition temperature. The gases above push the piston, provide the power stroke.

- **Ignition delay:** In diesel engine, ignition of fuel is not instantaneous. The time interval between start of fuel injection and its ignition is called ignition delay. If the ignition delay is long, it will lead to accumulation of more fuel into the cylinder. As a result, amount of combustion will be more leading to a significant increase in temp^{r} and generation of rattling sound. This is known as diesel Knocking.

- **Cetane number:**

Fuel	Cetane No.	Ignition delay
1. Cetane (n-hexadecane) $CH_3(CH_2)_{14}CH_3$	100	very short
2. 2-methyl napthalene	0	very long

For a particular fuel;

$$\text{Octane no.} \propto \frac{1}{\text{Cetane no.}}$$

Cetane number of a fuel is defined as the percentage of cetane in a mix of cetane and 2-methyl napthalene which has the same knocking property as the diesel engine.

Ignition delay order:

Alkane < Substituted alkane < cycloalkane < alkene < aromatics

Cetane number order:

Alkane > sub. alkane > Cycloalkane > alkene > aromatics

Additives such as Ethyl nitrile is used to increase the cetane number of the fuel.

* **Octane Number**

1. Percentage of isooctane in a mix of isooctane and n-heptane.
2. To grade quality of petrol fuel
3. Tetraethyl Lead is used to increase the octane number
4. Hydrocarbon which are good petrol fuel are bad diesel fuel.

Cetane number

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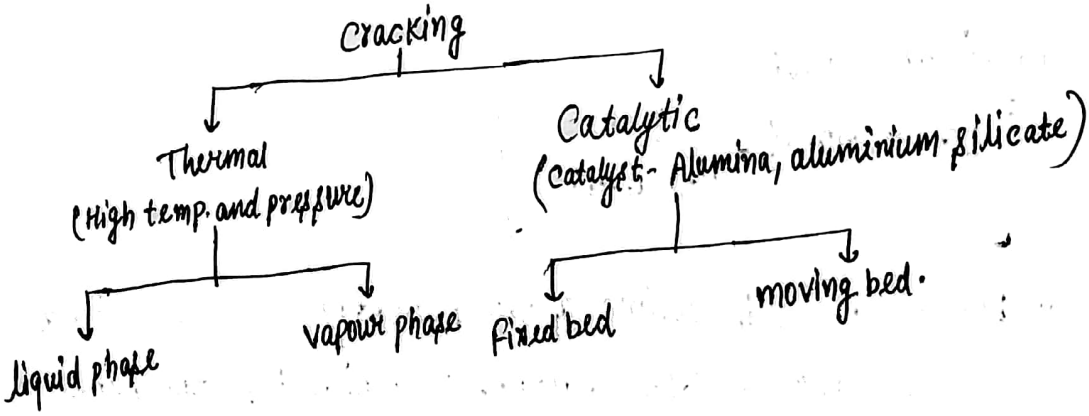
* **Cracking** :- Decomposition of higher molecular weight substances into several lower molecular weight substances.
It is done by Thermal or catalytic action.

$$C_{10}H_{22} \longrightarrow C_5H_{12} + C_5H_{10}$$
n-decane → n-pentane + pentene

Application:- Heavy oil produce gasoline on cracking.



Advantages of catalytic cracking over thermal cracking :-

i) Much milder reaction condition is required in Catalytic cracking.
ii) Better quality of petrol produced in catalytic cracking.
iii) Higher yield of petrol in catalytic cracking.
iv) Lower production cost in the case of catalytic cracking.

* **Aviation Gasoline** :- a) Used as a fuel in aeroplane.
b) Have high octane number.
It can be made by mixing branch chain hydrocarbon with unsaturated hydrocarbon.

* **Synthetic petrol** :- Petrol obtained from Syn gas (mixture of $CO + H_2$).
Fisher-Tropsch Process

* **Petrochemicals** :- Compounds derived from raw materials obtained from petroleum.

Primary source
Petroleum ⟶ secondary source
alkane
alkene
benzene
→ Process → Petrochemical

eg :- C_2H_5OH, CH_3COOH, polythene, etc.