Characteristics of hydrocarbons.

(1) **Knocking:** The metallic sound due to irregular burning of the fuel is termed as knocking.

"The greater the compression greater will be efficiency of engine." The fuel which has minimum knocking property is always preferred.

The tendency to knock falls off in the following order: Straight chain alkanes > branched chain alkanes > olefins > cyclo alkanes > aromatic hydrocarbons.

(2) **Octane number:** It is used for measuring the knocking character of fuel used in petrol engine. The octane number of a given sample may be defined as the percentage by volume of iso-octane present in a mixture of iso-octane and heptane which has the same knocking performance as the fuel itself.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \qquad \text{n-heptane; octane no.} = 0$$

$$CH_3 \qquad CH_3 \qquad CH_3 \qquad CH_3 - C-CH_2-CH-CH_3 \text{ ; Octane no.} = 100$$

$$CH_3 - C-CH_2-CH-CH_3 \text{ ; Octane no.} = 100$$

2, 2, 4-Trimethyl pentane or Iso-octane.

For example: a given sample has the knocking performance equivalent to a mixture containing 60% iso-octane and 40% heptane. The octane number of the gasoline is, therefore, 60.

Presence of following types of compounds increases the octane number of gasoline.

- (i) In case of straight chain hydrocarbons octane number decreases with increase in the length of the chain.
- (ii) Branching of chain increases the value of octane number
- (iii) Introduction of double bond or triple bond increases the value of octane number.
- (iv) Cyclic alkanes have relatively higher value of octane number.
- (v) The octane number of aromatic hydrocarbons are exceptionally high
- (vi) By adding gasoline additives (eg TEL)
- (3) **Antiknock compounds:** To reduce the knocking property or to improve the octane number of a fuel certain chemicals are added to it. These are called **antiknock compounds**. One such

compound, which is extensively used, is tetraethyl lead (TEL). TEL is used in the form of following mixture,

TEL = 63%, Ethylene bromide = 26%, Ethylene chloride = 9% and a dye = 2%.

However, there is a disadvantage that the lead is deposited in the engine. To remove the free lead, the ethylene halides are added which combine with lead to form volatile lead halides.

$$Pb + Br - CH_2 - CH_2 - Br \rightarrow PbBr_2 + CH_2 = CH_2$$

Ethylene bromide Volatile Ethylene

However, use of TEL in petrol is facing a serious problem of Lead pollution, to avoid this a new compound cyclopenta dienyl manganese carbonyl (called as AK-33-X) is used in developed countries as antiknocking compound.

(4) Other methods of improving octane number of gasoline

(i) **Isomerization**[Reforming]: By passing gasoline over $AlCl_3$ at 200 o C.

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{AlCl_{3}} CH_{3} \xrightarrow{CHC} H_{2}CH_{3}$$
Pentane (Octane number = 62)
$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{Isopentane} (Octane number = 90)$$
(iii) Alkylation: $CH_{3}CH + CH_{2} = CCH_{3} \xrightarrow{Isobutylen e} CH_{3}CCH_{2}CHCH_{3}$

$$CH_{3} \xrightarrow{Isobutylen e} CH_{3}CCH_{2}CHCH_{3}$$

$$CH_{3} \xrightarrow{Iso-octane} (Octane number = 100)$$
(iii) Aromatization: $CH_{3}(CH_{2})_{5}CH_{3} \xrightarrow{Pt/Al_{2}O_{3}} CH_{3}$

$$CH_{3} \xrightarrow{Iso-octane} (Octane number = 100)$$

$$CH_{3} \xrightarrow{Iso-octane} CH_{3} \xrightarrow{Toluene} CH_{3}$$

The octane no. of petrol can thus be improved.

- By increasing the proportion of branched chain or cyclic alkanes.
- By addition of aromatic hydrocarbons (BTX)
- By addition of methanol or ethanol.
- By addition of tetraethyl lead $(C_2H_5)_4Pb$
- (5) **Cetane number:** It is used for grading the diesel oils.

$$CH_3 - (CH_2)_{14} - CH_3$$
 Cetane \rightarrow cetane no. = 100

$$CH_2$$

$$Cetane no. = 0$$

$$\alpha$$
-Methyl naphthalene

The cetane number of a diesel oil is the percentage of cetane (hexadecane) by volume in a mixture of cetane and α -methyl naphthalene which has the same ignition property as the fuel oil

(6) **Flash point:** The lowest temperature at which an oil gives sufficient vapors to form an explosive mixture with air is referred to as flash point of the oil.

The flash point in India is fixed at $44^{\circ}C$, in France it is fixed at 35° C, and in England at 22.8° C. The flash point of an oil is usually determined by means of "**Abel's apparatus**".

Chemists have prepared some hydrocarbons with octane number even less than zero (e.g., n-nonane has octane number – 45) as well as hydrocarbon with octane number greater than 100 (e.g., 2, 2, 3 trimethyl-butane. has octane number of 124).

(7) **Petrochemicals:** All such chemicals which are derived from petroleum or natural gas called petrochemicals. Some chemicals which are obtained from petroleum are:

Hydrocarbons	Compounds derived
Methane	Methyl chloride, chloroform, methanol, formaldehyde, formic acid, freon, hydrogen for synthesis of ammonia.
Ethane	Ethyl chloride, ethyl bromide, acetic acid, acetaldehyde, ethylene, ethyl acetate, nitroethane, acetic anhydride.
Ethylene	Ethanol, ethylene oxide, glycol, vinyl chloride, glyoxal, polyethene, styrene, butadiene, acetic acid.
Propane	Propanol, propionic acid, isopropyl ether, acetone, nitromethane, nitroethane, nitropropane.
Propylene	Glycerol, allyl alcohol, isopropyl alcohol, acrolein, nitroglycerine, dodecylbenzene, cumene, bakelite.
Hexane	Benzene, DDT, gammexane.
Heptane	Toluene

Cycloalkanes	Benzene, toluene, xylenes, adipic acid.
Benzene	Ethyl benzene, styrene, phenol, BHC (insecticide), adipic acid, nylon, cyclohexane, ABS detergents.
Toluene	Benzoic acid, TNT benzaldehyde, saccharin, chloramine-T, benzyl chloride, benzal chloride.