Module-6:Fuels and Combustion

Contents:

- Calorific value – Significance and comparison between LCV and HCV. Measurement of calorific value using Bomb calorimeter and Boy's calorimeter including numerical problems. (2 hours)
- Controlled combustion of fuels - Air fuel ratio – minimum quantity of air by volume and by weight-Numerical problems- Three way catalytic converter- selective catalytic reduction of NO_X;
- Knocking in IC engines-Octane and Cetane number – Anti-knocking agents (1 hour)
- Fuel is a combustible substance, which on combustion produces a large amount of heat, which can be used for various domestic and industrial purposes.
- The process of combustion involves oxidation of carbon, hydrogen etc. of the fuels to CO_2, H_2O, and the difference in the energy of reactants and the products are liberated as large amount of heat energy which is utilized.

  $$\text{Fuel} + O_2 \text{ --------}\rightarrow \text{Products} + \text{Heat}$$

- The primary or main source of fuels are coal and petroleum oils, the amounts of which are dwindling day by day. These are stored fuels available in earth's crust and are generally called "fossil fuels".

#Calorific value of fuels

- The most important property of fuel to be taken into account is its calorific value or the capacity to supply heat. The calorific value of a fuel can be defined as "the total quantity of heat liberated when a unit mass or volume of the fuel is burnt completely".
- Units are Calorie/ Kilocalorie - Calorie is the amount of heat required to raise the temperature of one gram of water through one degree centigrade.
- **#Higher or Gross Calorific Value (HCV or GCV):** Usually, all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted to steam.
- If the products of combustion are condensed to room temperature (15°C or 60°F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross c;alorific value".
- So gross or higher calorific value may be defined as "the total amount of heat produced when one unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature".

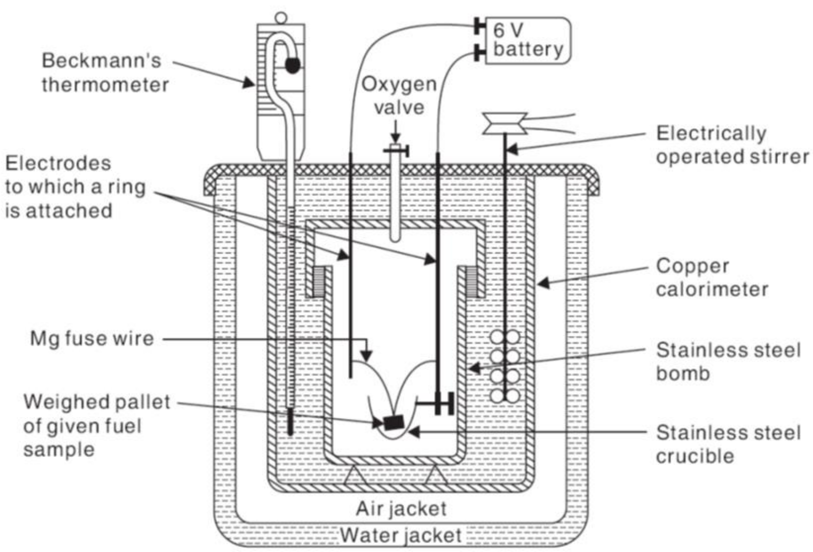
- **Lower or Net Calorific Value:** In actual use of fuel, the water vapour and moisture etc are not condensed and escapes as such along with hot combustion gases. Hence a lesser amount of heat is available. So, net or lower calorific value may be defined as "the net heat produced when unit mass / volume of the fuel is burnt completely and the products are permitted to escape".
- Net or lower calorific value can be found from GCV value

  NCV = GCV - Latent heat of water vapour formed

  = GCV - Mass of hydrogen x 9 x latent heat of steam
- 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of steam is 587 k cal / kg or 1060 B. Th. U. / *l*b of water vapour formed at room temperature. (ie 15°C).

Determination of Calorific Value

Bomb calorimeter



Calculation

m = mass of fuel pellet (g)

W = mass of water in the calorimeter (g)

w = water equivalent of calorimeter (g)

t1 = initial temperature of calorimeter.

t2 = final temperature of calorimeter.

HCV = gross calorific value of fuel.

$$L = HCV = \frac{(W + w)\,(t_2 - t_1)}{m} \text{ cal/gm.}$$

Water Equivalent of the calorimeter is determined by burning a fuel of known calorific value (benzoic acid (HCV = 6,325 kcal/kg) and naphthalene (HCV = 9,688 kcal/kg)

If H is the percentage of hydrogen in fuel,

the mass of water produced from 1 g of fuel = (9/100)×H

= 0.09 H

Heat taken by water in forming steam = 0.09 H× 587 cal

(latent heat of steam = 587 cal/kg)

LCV = HCV – Latent heat of water formed

$$LCV = \left[HCV - \frac{9}{100}\,H \times 587\right] \text{ kcal/kg.}$$

$$= [HCV - 0.09\ H \times 587] \text{ kcal/kg.}$$

1. 0.72 gram of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3° to 29.1°C. If the calorimeter contains 250 grams of water and its water equivalents is 150 grams, calculate the HCV of the fuel. Give your answer in KJ/Kg.

Solution. Here x= 0.72 g, W = 250g, t_1 = 27.3°C, t_2 = 29.1°C.

$$\text{HCV of fuel (L)} = \frac{(W + w)\,(t_1 - t_2)}{x}\ \text{Kcal/kg}$$

$$= \frac{(250 + 150) \times (29.1-27.3)}{0.072}\ \text{kcal/kg} = 1{,}000 \times 4.2\ \text{kJ/Kg} = 4{,}200\ \text{kJ/kg}$$

2. On burning 0.83 of a solid fuel in a bomb calorimeter , the temperature of 3,500g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385.0g of and 587.0 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific value.

Solution. Here wt. of fuel (x) = 0.83 g of ; wt of water (W) = 3,500 g; water equivalent of calorimeter (w) = 385 g ; (t_2 - t) = (29.2°C - 26.5°C) = 2.7°C ; percentage of hydrogen (H) = 0.7% ; latent heat of steam = 587 cal/g

$$\text{Gross calorific value} = \frac{(W + w)\,(t_1 - t_2)}{x}\ \text{cal/g}$$

$$= \frac{(3{,}500 + 385) \times 2.7}{0.83} = 12{,}638\ \text{cal/g}$$

$$\text{NCV} = [\text{GCV} - 0.09\ H \times 587]$$

$$= (12{,}63\,8 - 0.09 \times 0.7 \times 587)\ \text{cal/g}$$

$$= (12{,}638 - 37)\ \text{cal/g} = 12{,}601\ \text{cal/g}$$

Corrections: For accurate results the following corrections are also incorporated:

1. **Fuse wire correction**
2. **Acid correction**
3. **Cooling correction**

Fuse wire correction:

Heat liberated during sparking should be subtracted from calorific value

~ As Mg wire is used for ignition, the heat generated by burning of Mg wire is also included in the gross calorific value. Hence, this amount of heat has to be subtracted from the total value

Acid correction:

Fuels containing Sulphur and Nitrogen if oxidized, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions)

Acid Correction: During combustion, sulphur and nitrogen present in the fuel are oxidized to their corresponding acids under high pressure and temperature.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta H = -144{,}000 \text{ Cal}$$

$$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3 \qquad \Delta H = -57{,}160 \text{ Cal}$$

The corrections must be made for the heat liberated in the bomb by the formation of H_2SO_4 and HNO_3. The amount of H_2SO_4 and HNO_3 is analyzed by washings of the calorimeter.

For each ml of 0.1 N H_2SO_4 formed, 3.6 calories should be subtracted.

For each ml of 0.01 HNO_3 formed, 1.43 calories must be subtracted.

Cooling correction:

The rate of cooling of the calorimeter from maximum temperature to room temperature is noted. From this rate of cooling (i.e., dt°/min) and the actual time taken for cooling (X min) then correction (dt × X) is called cooling correction and is added to the (t2 . t1) term.

If the time taken for the water in the calorimeter to cool down from the maximum temperature attained, to the room temperature is x minutes and the rate of cooling is dt/min, then the cooling correction = x × dt. This should be added to the observed rise in temperature.

Therefore, Gross calorific value

=(W+w)(t_2-t_1+Cooling correction)-[Acid+ fuse corrections] / Mass of the fuel.

$$GCV = \frac{(W+w)\,(t_2 - t_1 + \text{Cooling Correction}) - (\text{Acid} + \text{Fuse Correction})}{\text{Mass of the fuel } (x)}$$

3. A sample of coal contains C =93%; H =6% and ash = 1%. The following data were obtained when the above coal was tested in bomb calorimeter.

Wt. of coal burnt =0.92g
Wt. of water taken =550g
Water equivalent of calorimeter =2,200g
Rise in temperature =2.42 °C
Fuse wire correction =10.0 cal
Acid correction =50.0 cal

Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580 cal/g.

Solution: Wt. of coal sample (x) = 0.92 g; wt. of water (W) =550 g;
water equivalent of calorimeter (w) = 2,200g;
temperature rise (t_2-t_1) = 2.42 °C;
acid correction = 50.0cal;
fuse wire correction = 10.0 cal;
latent heat of steam = 580 cal/g;
percentage of H =6%

$$\text{GCV} = \frac{(W + w)\ (t_1 - t_2) - [\text{acid+fuse corrections}]}{x}$$

$$= \frac{(550+2,200) \times 2.42 - [50+10]\ \text{cal}}{0.92\text{g}}$$

$$= 7,168.5\ \text{cal/g.}$$

$$\text{NCV} = [\text{GCV} - 0.09\ \text{H} \times \text{latent heat steam}]$$

$$= (7168.5 - 0.09 \times 6 \times 580)\ \text{cal/g}$$

$$= 6855.3\ \text{cal/g}$$

Boy's Calorimeter

It is used for measuring the calorific value of gaseous (or) liquid fuels.

Principle

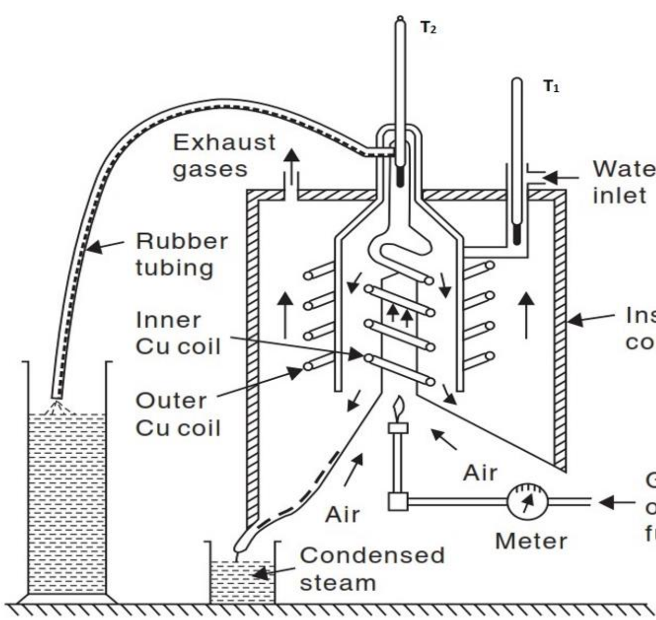
- A known volume of gaseous fuel sample is burnt in the combustion chamber of a Boy's calorimeter.
- The released heat is quantitatively absorbed by cooling water, circulated through copper coils surrounding the combustion chamber.
- The mass of cooling water and its rise in temperature are noted.
- The mass of water produced by condensation of steam is calculated.
- The calorific value of the fuel sample is then calculated from these data.

Construction

Boy's calorimeter consists of a combustion chamber surrounded by water tube with two thermometers T_1 and T_2 attached. There is a burner in the chamber, which is connected to a gas tube.

Working

- **A known volume of water is passed through the tubes.**
- **The initial temperature is noted when the two thermometers show the same constant temperature.**
- **A known volume of the gas (measured using a meter) is passed through the tube and burnt in the combustion chamber.**
- **The heat liberated is absorbed by the water in the tubes.**
- **The final temperature of water is noted.**
- **The gaseous products are cooled and condensed into a measuring jar.**



Boy's gas calorimeter

Calculation

Volume of gas burn at STP in certain time (t)= V
Mass of the cooling water used in time t = W
Temperature of inlet water = T_1
Temperature of outlet water = T_2
Mass of steam condensed in time t in graduated cylinder = m
Higher calorific value of fuel = L
Specific heat of water = S
Heat absorbed by circulating water = W(T_2-T_1)×Specific heat of water (s)
Heat produced by combustion of fuel = VL
Thus

$$VL = W(T2-T1)\times S$$

$$\text{Gross calorific value} = W \times S \times \frac{(T_2 - T_1)}{V}$$

$$\text{LCV} = \left[\text{L} - \frac{\text{amount of water collected x latent heat}}{\text{V}} \right]$$

Dulongs Formula

The approximate calorific value of a fuel can be determined by knowing the amount of constituents present:

Gross or higher calorific value (HCV) from elemental constituents of a fuel.

H = 34500 kcal/kg; C = 8080 kcal/kg; S = 2240 kcal/kg

Oxygen present in the fuel is assumed to be present as water (fixed hydrogen).

Available Hydrogen = Total hydrogen - Fixed hydrogen
= Total hydrogen - 1/8 mass of oxygen in fuel.

Dulongs formula for calorific value from the chemical composition of fuel is,

$$HCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{0}{8}\right) + 2240\,S\right] \text{kcal/kg}$$

COMBUSTION

- Calculation of air quantities
- ✓ Substances always combine in definite proportions.

$$\begin{array}{lll} C(s) + O_2(g) & \longrightarrow & CO_2(g) \\ 12 \quad 32 & & 44 \end{array}$$

- ✓ Air contains 21% of oxygen by volume & 23% of oxygen by mass.

$1kg$ of oxygen is supplied by $\frac{1x100}{23}$ = 4.35kg of air

$1m^3$ of oxygen is supplied by $\frac{1x100}{21}$ = 4.76 m^3 of air

- ✓ 28.94g/mol is taken as the molecular mass of air
- Since air has 23% by weight or 21% by volume of oxygen
- Minimum weight of air needed for complete combustion = Net O_2 x 100/23g
- Minimum volume of air needed for complete combustion = Net O_2 x 100/21g

Procedure for Combustion Calculations

Combustion equation	Wt of Oxygen needed	Vol. Of Oxygen needed
$C + O_2 \longrightarrow CO_2$ x g or m3	x.32/12	x X 1
$H_2 + 0.5O_2 \longrightarrow H_2O$ y g or m3	y x 16/2	y X 0.5
$CO + 0.5O_2 \longrightarrow CO_2$ Zg or m3	Z x 16/28	Z x 0.5
$S + O_2 \longrightarrow SO_2$ Pg or m3	p x 1 x 32/32	P X 1
$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O$ q g or m3	qx2x32/16	q X 2
$C_2H_6 + 3.5O_2 \longrightarrow CO_2 + 3H_2O$ r g or m3	r x 3.5 x 32/30	r X 3.5

Q.1. How much air is required to burn 1kg of pure Carbon?

Solution: The MWt of O_2 is 32. This reacts with C, MWt of 12.

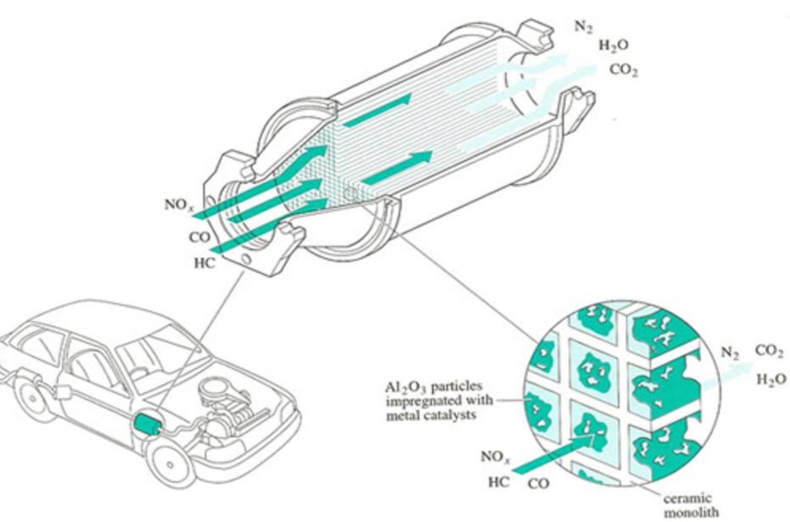
$$\begin{array}{lll} C(s) + & O_2(g) & — \; CO_2(g) \\ 12 & 32 & 44 \\ 1000\,g & m_{Oxygen} & \end{array}$$

$$m_{Oxygen} = \frac{1000 \times 32}{12} = 2667 \text{ g or } 2.667 \text{ kg of } O_2$$

But, air contains only 23 % of O_2.

Mass of air required to burn 1 kg of pure coal = $\frac{100 \times 2.667}{23}$ = 11.59 kg

The three-way catalytic converter

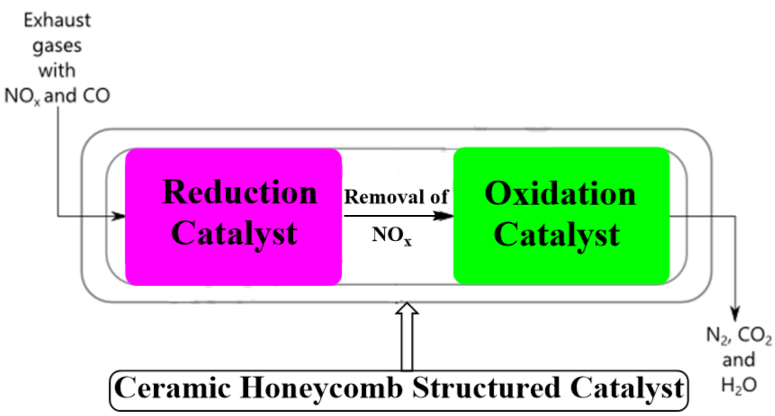


Components

- The current three-way catalyst is generally a multicomponent material, containing the precious metals rhodium, platinum and (to a lesser extent) palladium, ceria (CeO_2), γ-alumina (Al_2O_3), and other metal oxides.
- It typically consists of a ceramic monolith of cordierite ($2Mg.2Al_2O_3.5SiO_2$) with strong porous walls enclosing an array of parallel channels.
- For example, Cordierite is used because it can withstand the high temperatures in the exhaust, and the high rate of thermal expansion encountered when the engine first starts – typically, the exhaust gas temperature can reach several hundred degrees in less than a minute.
- The reduction catalyst is made of platinum and rhodium while the oxidation catalyst is made of platinum and palladium. Both the catalysts have a ceramic honeycomb structure.

Working of 3-way Catalytic Converter

A three-way catalytic converter makes use of two catalysts to convert harmful gases to harmless gases. They are: **Reduction Catalyst** & **Oxidation Catalyst**



Stage 1 – Reduction Catalyst:

- The exhaust gases are first sent over the reduction catalyst (which is made of platinum and rhodium). It converts oxides of nitrogen (NO_x) to nitrogen (N_2) and oxygen (O_2).

$$2NO \rightarrow N_2 + O_2$$

$$2NO_2 \rightarrow N_2 + 2O_2$$

Stage 2 – Oxidation Catalyst:

- Exhaust gases that are free of oxides of nitrogen (NO_x) are then sent over the oxidation catalyst (made of platinum and palladium). The oxidation catalyst coverts carbon-monoxide (CO) and hydrocarbons (HC) in the gases into carbon-di-oxide (CO_2) and water (H_2O).

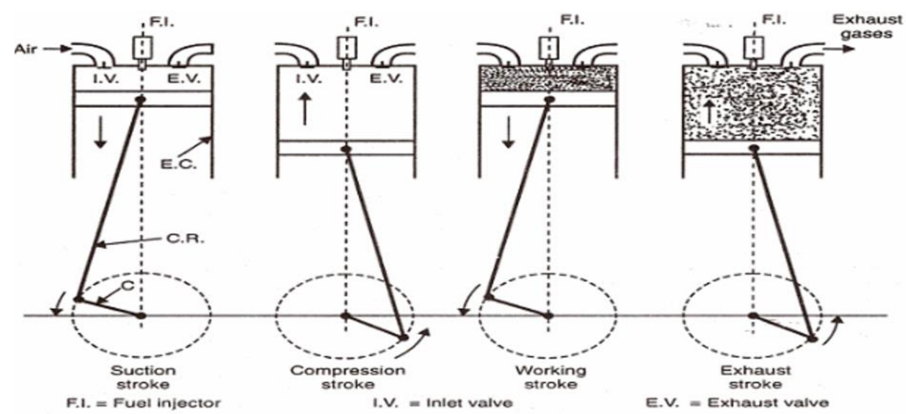
$$2CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$

Knocking:

- In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel.
- After the initiation of the combustion reaction by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture, thereby the expanding gas drives the piston down the cylinder.
- The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression-stroke of the piston is known as the 'compression ratio'.
- The efficiency of an internal combustion engine increases with the compression ratio.
- Compression ratio (CR) is defined as the ratio of the cylinder volume (V1) at the end of the suction stroke to the volume (V2) at the end of the compression stroke of the piston.
- V1 being greater than V2, the CR is >1.
- The CR indicates the extent of compression of the fuel-air-mixture by the piston.
- However, successful high compression ratio is dependent on the nature of the constituents present in the gasoline used.
- In certain circumstances, due to the presence of some constituents in the gasoline used, the rate of oxidation becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously producing an explosive violence, known as 'knocking'.

The knocking results in loss of efficiency, since this ultimately decreases the compression ratio



Chemical structure and knocking

- The tendency of fuel constituents to knock is in the following order. Straight - chain paraffins > branched - chain paraffins (isoparaffin) > olefins > cyclo paraffins (naphthenes) > aromatics.

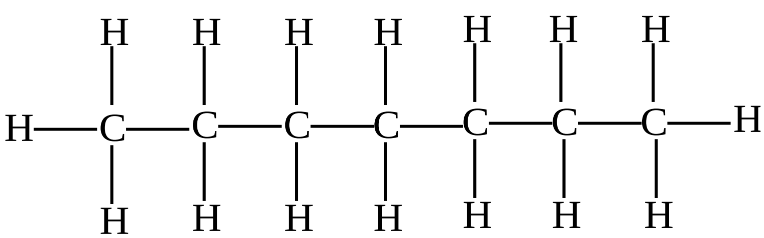
Octane number

- The most common way of expressing the knocking characteristics of a combustion engine fuel is by 'octane number', introduced by Edger. It has been found that n-heptance, knocks very badly and hence, its anti-knock value has arbitrarily been given zero.

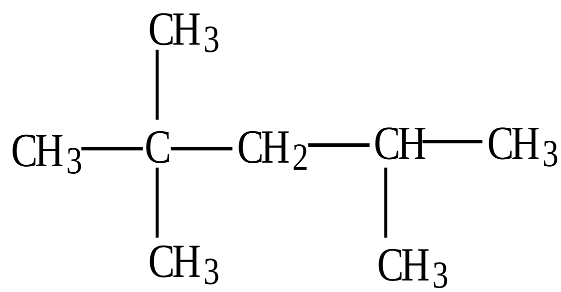
- Octane number is equal to the percentage by volume of iso-octane (2,2,4-trimethyl pentane) in a mixture of n-heptane and iso-octane having the same knocking tendency compared to the sample of gasoline being tested;
- Iso-octane has the best antiknocking properties and assigned an octane number of 100 whereas n-heptane has poor antiknocking property and assigned an octane number of zero.

- The hydrocarbons present influence the knocking properties of gasoline which vary according to the series:

  straight chain paraffin > branched chain paraffin > olefin > cycloparaffin > aromatics.
- The fuel which has same knocking tendency with the mixture having 80% iso-octance has octane number 80.



n-heptane



Isooctane

Improvement of anti-knock characteristics of a fuel:

- The octane number of many otherwise poor fuels can be raised by the addition of tetra ethyl lead $(C_2H_5)_4Pb$ or TEL and diethyl telluride $(C_2H_5)_2Te$. In motor spirit (Motor fuel) about 0.5ml and in aviation fuel 1.0 - 1.5ml of TEL is added per litre of petrol.

- TEL is converted into a cloud of finely divided lead and lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxide molecules formed, thereby slowing down the chain oxidation reaction and thus decreasing the chances of any early detonation.

- However deposit of lead oxide is harmful to the engine life. In order to help the simultaneous elimination of lead oxide formed from the engine, a small amount of ethylene dibromide (or ethylene dichloride) is also added to petrol.

- The added ethylene dibromide removes lead oxide as volatile lead bromide along with the exhaust gases. The presence of sulphur compounds in petrol reduces the effectiveness of the TEL. TEL is more effective on saturated hydrocarbons than on unsaturated ones.

Anti knocking Agents:

- Anti Knocking agents are the additives added in small quantities in petrol engine to reduce the knocking tendency.

Very much known anti knock agent was tetraethyl lead (TEL), but the usage of this is associated with the Environmental and Health issues of **Lead**

Types of Anti-knocking agents:

- *Broadly, there are three major groups of anti-knocking agents :*
- **1.** Aromatics, **2**. Oxygenates and **3.** Organometallic compounds

1. Aromatics - **Toluene and Xylene** (non-carcinogenic)

Benzole (BTEX)**– A mixture of Benzene, Toluene and Xylene is used as an anti-knocking agent**

The higher the **Toluene** content the more effective is its antiknock value but with in certain limits

- **2**. Oxygenates - **MTBE** (methyl tertiary butyl ether) and **ETBE** (ethyl tertiary butyl ether)
- **3.** Organometallic compounds –

MMT (methyl cyclopentadieny manganese tri-carbonyl), **Ferrocene** (dicyclopentadienyl iron), **nickel carbonyl, TEL** (tetra ethyl lead) or **TML** (tetra methyl lead). They are all toxic in nature. But **Ferrocene** is safer than **TEL/ TML**.

Iron pentacarbonyl has been found to be a strong flame speed inhibitor in oxygen based flames.

- **Other additives:**
- Oxidation inhibitors - 2,4 - ditertiary butyl - 4 - methyl phenol.
- Rust inhibitors - Organic compounds of phosphorus or antimony.
- Ignition control additives - tricresyl phosphate which suppresses pre-ignition of the fuel due to glowing deposits on spark plug or a hot spot on the cylinder wall.

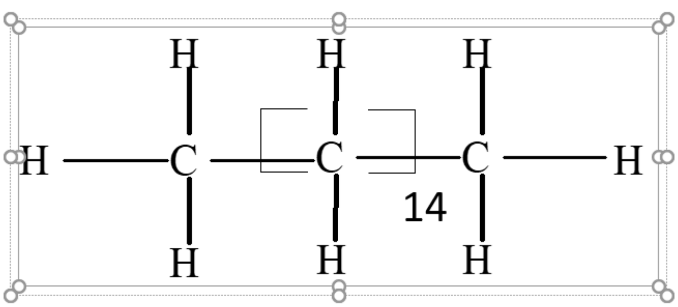
Diesel Engine Fuels: Characteristics of an ideal diesel oil

- It should have low spontaneous ignition temperature.
- It should have very little sulphur, aromatic and ash content.

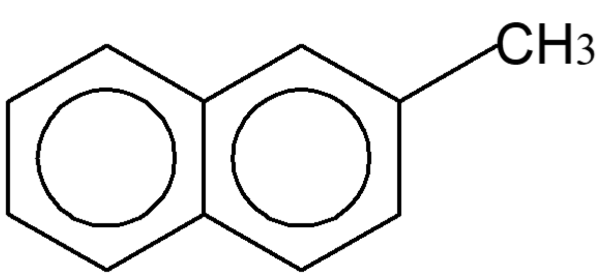
~The ignition lag should be as short as possible

- **Knocking in Diesel Engines:** In a diesel engine, the fuel is exploded not by a spark, but by the application of heat and pressure. In the cycle of operations of a diesel engine, air is first drawn into the cylinder and compressed.
- Towards the end of the compression stroke, the fuel (diesel oil) is injected as a finely-divided spray into air in the cylinder heated to about 500°C by compression.

- The oil absorbs the heat from the air and if it attains its ignition temperature the oil ignites spontaneously. The pressure of the gases is further increased by the heat accompanying the ignition of the oil.
- The piston is pushed by the expanding gases and this constitutes the power stroke.
- Fuel feed and ignition continue during this down stroke. The fuel injection stops at the exhaust stroke.
- **Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels.**
- The main characteristic of diesel engine fuel is that it should easily ignite below compression temperature.
- There should be as short an induction lag as possible. This means that it is essential that the hydrocarbon molecules in a diesel fuel should be as far as possible the straight-chain ones with a minimum admixture of aromatic and side-chain hydrocarbon molecules.
- The suitability of a diesel fuel is determined by its cetane value, which is the percentage of hexadecane in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel sample, under the same set of conditions.
- The cetane number of a diesel fuel can be raised by the addition of small quantity of certain "pre-ignition dopes" like alkyl nitrites such as ethyl nitrite, iso-amyl nitrite, acetone peroxide.



***n*-Hexadecane (Cetane No. = 100)**



2-Methyl naphthalene (Cetane No. = 0)

Ignition quality decreases among hydrocarbons is as follows

- n-alkanes > naphthalenes > alkenes > branches alkanes > aromatics

- Cetane number decreases
- Ignition quality decreases
- Ignition delay increases

- Diesel – Index: On API (American petroleum Institute) scale, the quality of a diesel fuel is, sometimes, indicated by diesel-index number which is

$$\text{D. I} = \frac{\text{Specific gravity (API)} \times \text{Aniline Point } (^\circ\text{F})}{100}$$

- The higher the diesel-index number the better is the diesel fuel. D. I. = Cetane number + 3.