MODULE 6

Calorific value - Definition of LCV, HCV. Measurement of calorific value using bomb calorimeter and Boy's calorimeter including numerical problems.

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 - Antiknocking agents.

Fuels

- Fuel is a combustible substance, containing carbon as the main constituent, which on proper burning gives large amount of heat that can be used for domestic and industrial purposes
- During combustion of a fuel, atoms of C and H combine with oxygen to give CO_2 and H_2O
- These compounds have lesser energy than the fuel and hence the energy released during combustion is the difference in energy of the reactant and the products formed

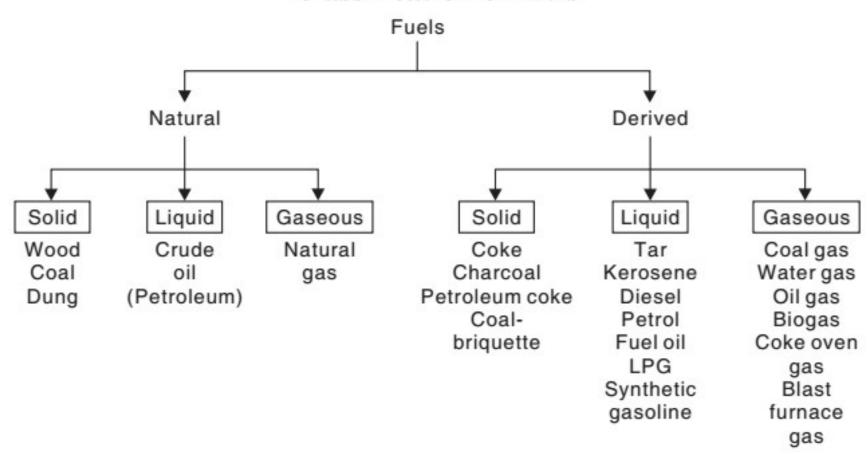
Fuel +
$$O_2$$
 Products + Heat

- 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
- Expressed in cal/g or kcal/kg

Characteristics of a good fuel

- It should have higher calorific value.
- Moderate ignition temperature.
- Low moisture content.
- Low non-combustible matter content
- A good fuel should burn with moderate rate of combustion.
- Products of combustion should not be harmful and polluting
- Should not undergo spontaneous combustion, but the combustion process should be easily controllable
- Should burn efficiently without much smoke

Classification of fuels



Units of Calorific Value

- **1. Calorie** Calorie is the amount of heat required to raise the temperature of one gram of water through one degree centigrade.
- **2. Kilocalorie** This is the unit of metric system and is equal to 1000 calories.

This may be defined as "the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade".

Thus 1 kcal = 1000 cal.

3. British thermal unit (B. Th. U.) - This is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit". This is English system unit.

1 B. Th. U. = 252 cal = 0.252 k cal. 1 k cal = 3.968 B. Th. U.

4. Centigrade Heat Unit (C. H. U.) - This is the "quantity of heat required to raise the temperature of one pound of water through one degree centigrade".

Thus, 1 k cal = 3.968 B. Th. U. = 2.2 C. H. U.

1 calorie = 4.187 Joule

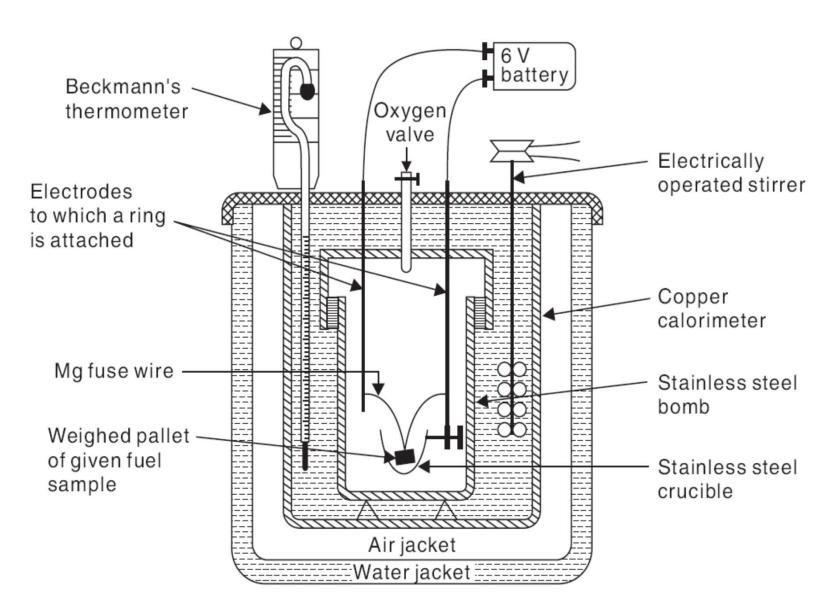
GCV/HCV- Gross / Higher calorific value

- "Amount of heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion have been cooled to room temperature".
- Most of the fuels used are hydrocarbon based.
- When the products are cooled to room temperature, the steam present condenses, releasing its latent heat of vapourisation
- If the products of combustion are condensed to room temp., the latent heat
 of condensation of steam also gets included in the measured heat.
 Hence higher (or) gross calorific value

NCV/LCV- Net / Lower calorific value

- Amount of heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion have been allowed to escape".
- In practice, water vapor are not condensed but allowed to escape. Hence lesser amount of heat is available.
- LCV = HCV Latent heat of water vapor produced
- = HCV (Mass of hydrogen in the fuel x 9 x Latent heat of steam)

Determination of Calorific Value by Bomb calorimeter



Bomb calorimeter

- Used to find calorific value of solid and liquid fuels
- The bomb consists of lid which can give a gas-tight seal
- The lid also has two electrodes and an oxygen inlet valve
- To one of the electrodes a ring is attached in which a crucible is supported
- The bomb is placed in a copper calorimeter
- A known mass of fuel is completely burnt in excess of oxygen and heat liberated is absorbed by the surrounding water and the brass calorimeter
- The increase in temperature of the calorimeter and water is noted
- Calorific value is calculated based on fact that heat lost by burning the fuel is equal to the heat gained by the water and the calorimeter
- The heat quantity calculated is GCV because the products of combustion remain inside the calorimeter and brought down to ambient temperature

Calculation

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

$$H_2 + \frac{1}{2} O_2$$
 $H_2 O_2$ 18 kg

Where

m = mass of fuel pellet (g)

W = mass of water in the calorimeter (g)

w = water equivalent of calorimeter (g)

 t_1 = initial temperature of calorimeter.

 t_2 = final temperature of calorimeter.

HCV = gross calorific value of fuel.

S = specific heat capacity of water

- The water equivalent of the calorimeter is related to its heat capacity, is determined by burning a fuel of known calorific value. E.g benzoic acid (HCV = 6,325 kcal/kg) or naphthalene (HCV = 9,688 kcal/kg)
- The NCV of a fuel can be calculated if the percentage of hydrogen in the fuel is known
- Since 2 kg of H produces 18 kg of steam, x kg would produce 9x kg of steam
- If 100 kg of fuel contains x kg of H, then 1 kg of the fuel would produce 0.09x kg of steam
- Latent heat of steam is 587 kcal/kg
- Hence NCV = HCV latent heat of water formed = HCV - 0.09x (587) kcal/kg

5. Corrections

Fuse wire correction: Heat liberated during sparking should be subtracted from the total heat obtained.

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).

Cooling correction: time taken to cool water in calorimeter from max temperature to room temperature is noted. From the rate of cooling (dt °/min) and actual time for cooling (t min) the cooling correction of dt x t is added to the raise in temperature (to account for heat transfer from calorimeter to its environment)

$$L = HCV = \frac{(W+w).S.(t_2 - t_1 + cooling\ correction) - (Acid+fuse\ correction)}{m} \quad \text{cal/g}$$

$$LCV = \left[HCV - \frac{9}{100} \text{ H} \times 587\right] \text{ kcal/kg.}$$
$$= [HCV - 0.09 \text{ H} \times 587] \text{ kcal/kg.}$$

Amount of Hydrogen content (kg)in fuel

Example 1. A sample of coal contains:

$$C = 93\%$$
, $H = 6\%$ and $ash = 1\%$

Calculate the gross and net calorific V value of the coal from the following data:

Weight of coal burnt (m) = 0.92 g

Weight of water taken (w) = 550 g

Water equivalent of bomb calorimeter (W) = 2,200 g.

Rise in temperature $(t_2 - t_1) = 2.42$ °C; Fuse wire correction = 10 cal.

Acid correction = 50 cal

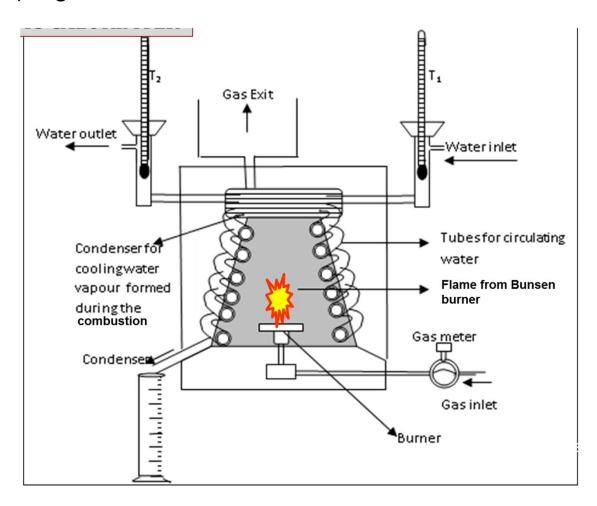
Sol. HCV =
$$\frac{(W + w) (t_2 - t_1) - [acid + fuse] correction}{m}$$
$$= \frac{(2,200 + 530) \times 2.42 - [50 + 10]}{0.92} cal/g$$
$$= 7168.5 cal/g$$

Example 3. On burning 0.83 g of a solid fuel in bomb calorimeter, the temperature of 3,500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385 g and 587 cal/g, respectively. If the fuel contains 0.77% H, calculate HCV and NCV.

$$\begin{split} \text{HCV} &= \frac{(\text{W} + w) \ (t_2 - t_1)}{m} * \text{S} \\ &= \frac{(385 + 3500) \ (29.2 - 26.5) * 1}{0.83} = 12638 \ \text{cal g}^{-1} \\ \text{NCV} &= (\text{HCV} - 0.09 \ \text{H} \times \text{L}) \ \text{cal g}^{-1} \\ &= (12638 - 0.09 \times 0.7 \times 587) \ \text{cal g}^{-1} = 12601 \ \text{cal g}^{-1}. \end{split}$$

Boys gas calorimeter

- The Boys gas calorimeter is a simple and effective means of measuring the calorific values of gaseous fuels.
- Named after an English physicist, Sir Charles Vernon Boys (1855-1944).
- It is the standard piece of equipment used to calculate the Higher Calorific (HCV) and the Lower Calorific (LCV) of gaseous fuels



The Boys calorimeter consists of following

- **Bunsen Burner**: special type of Burner attached at the bottom. It can be pulled out or pushed up in combustion chamber during the combustion process.
- Gas meter: It is used to measure the volume of gas burning per unit time. This is attached
 with manometer fitted with the thermometer so that pressure and temperature of the gas
 before burning can be read.
- Pressure governor: It can control the quantity of gas supplied at any given pressure.
- Gas Calorimeter/ Combustion chamber: It is a vertical Stainless steel cylinder, which is surrounded by annular space for heating water and interchange coils. The entire set up is covered by an outer jacket in order to reduce the heat loss by radiation and convection.

- Circulation of water and burning fuel is continued at constant rate for about 15 mins for initial warm up period
- The rates of fuel burning and water circulation are controlled so that the water exiting the apparatus is at atmospheric pressure
- Once the steady conditions are established, then the following values are noted
- The volume of gaseous fuel burnt (V) at given temperature and pressure in certain period of time (t)
- The quantity of water (W, Kg) passing through the annular space during the same interval
 of time
- The steady rise in temperature (T₂-T₁)
- The mass of water (steam) condensed (in Kg) in the outlet water.

Calculation:

Higher calorific value of fuel = L

Volume of gas burnt at STP in certain time (t)= V

Mass of the cooling water used in time t = W

Specific heat of water = S = 4.186 J/g. K or 1 cal/g.K

Temperature of inlet water = T_1

Temperature of outlet water = T_2

Mass of steam condensed in time t in graduated cylinder = m

Heat absorbed by circulating water = $W(T_2-T_1)\times Specific$ heat of water (s) Heat produced by combustion of fuel = V*L

Thus

$$VL = W(T_2 - T_1) \times S$$

$$HCV(L) = W(T2-T1) \times S/V$$

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

$$LCV = \left[L - \frac{m * 587}{v}\right] \text{ kcal/m}^3$$

 $1 \text{ cm}^3 \text{ of water} = 1 \text{ g of water}$

Problem-1

Calculate the gross calorific value and net calorific value of a gaseous fuel, 0.011m³ of which when burnt raised the temperature of 3.1kg of water by 8.2K. Specific heat of water is 4.186 kJ kg⁻¹K⁻¹. Latent heat of steam is 2.45 kJ kg⁻¹. The volume of water collected is 6.1cm³.

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V = volume of the gas burnt = 0.011 \text{ m}^3 = 1.1 \text{ x} 10^4 \text{ cm}^3

W = mass of water = 3.1 \text{ kg}

t_2- t_1 = rise in temperature = 8.2 \text{ K}

s = specific heat of water = 4.186 \text{ kJ kg}^{-1}\text{K}^{-1}

v = volume of water collected = 6.1 \text{ cm}^3 = 6.1\text{E} \cdot 6 \text{ m}^3

L = W(T2-T1)*S/V = 3.1*8.2*4.186/1.1 \text{ x} 10^4 = 9.65 \text{ J/cm}^3

NCV = L - (v*587*4.186/V) = 9.65 - (6.1*587*4.186/1.1 \text{ x} 10^4)

= 9.65 - 1.36 \text{ kJ/cm}^3

= 8.29 \text{ J/cm}^3
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Problem-2

During the determination of calorific value of a gaseous fuel by Boy's Calorimeter.

The following results are obtained

Vol. of gaseous fuel burnt at NTP = 0.093 m^3 V

Weight of water used for cooling the combustion products = 30.5 kg W

Weight of steam condensed = $0.031 \text{ kg } \mathbf{v}$

Temp. of inlet water = 26.1°C T1

Temp. of outlet water = 36.5° C **T2**

Determine the gross and net calorific value of the gaseous fuel per cubic meter at NTP provided that the heat liberated in condensation of water Vapor is 587cal/g

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L = W(T2-T1)*S/V

= 30.5*(36.5 - 26.1)*1/0.093 = 3,410 \text{ kcal/m}^3

NCV = L - (v*0.587*4.186/V) = 3,410 - (0.031*587*1/0.093)

= 3,410 - 195.7

= 3,214.3 \text{ kcal/m}^3
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Combustion process

Combustion is an exothermic chemical reaction accompanied by increase of heat

E.g
$$C + O_2 \longrightarrow CO_2 (g) + 97 \text{ Kcal}$$

- The gaseous products mainly are CO, CO_2 , N_2 , O_2 , SO_2 , H_2O which are known as flue gases
- Availability of oxygen is the most important parameter controlling the efficiency of a combustion process
- Calculation of minimum amount of air required to completely combust is essential
- Air contains 23% by weight and 21% by volume of oxygen
- i.e., 23 kg of Oxygen is present in 100 kg of air by weight
- And 21 m³ of Oxygen is present in 100 m³ of air by volume
- 22.4liters of any gas at NTP (0°C and 760 mm Hg) has mass equal to its 1mol (gram molecular weight)
- 22.4 L of O₂ at NTP will have a mass of 32 g
- 22.4 m³ of O_2 at NTP = 32 kg of O_2 (1m³ = 1000 lit)

Combustion of Carbon

•
$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

12 32 44

- 12 kg of carbon requires 32 kg of oxygen for complete combustion
- \Rightarrow 1 kg of carbon requires 32/12 kg of oxygen = 2.66 Kg of oxygen

By weight:

23 Kg of O_2 is \equiv 100 Kg of air 2.66 Kg of oxygen will be present in = 100/23 *(2.66) = 11.56 Kg of air

By Volume:

32 Kg weight of $O_2 = 22.4 \text{ m}^3$ of O_2 So 2.66 Kg of $O_2 = 22.4/32 * (2.66) \text{ m}^3 = 1.86 \text{ m}^3$ of Oxygen We know that 21m^3 of $O_2 = 100 \text{ m}^3$ of air So, 1.86m^3 of $O_2 = 100/21*(1.86 *C) \text{ m}^3 = 8.87\text{m}^3$ of air

Combustion of Hydrogen

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$
4 32 36

4 Kg hydrogen requires 32 kg oxygen for combustion

H kg Hydrogen in the fuel requires oxygen for complete combustion = 32/4 * H

From the total amount of hydrogen In the fuel part of hydrogen are non combustible in the form of water

8 parts of oxygen combines with 1 part of hydrogen

The amount of hydrogen available for combustion = (H-O/8)

Hence oxygen required for combustion of hydrogen = 32/4 * (H-O/8)

Combustion of Sulphur

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

32 32 64

32Kg of Sulphur requires 32 kg oxygen for combustion

S kg sulphur in the fuel requires oxygen for complete combustion = 32/32 *S

On combining the three eqns.,

the theoretical oxygen requirement for the combustion of C, H, and S

$$= 32/12 * C + 8 (H-O/8) + S in Kg$$

Air contains 23 % by weight of oxygen and 21 % by volume of oxygen

Minimum weight of air required for combustion = 100/23 * [32/12* C+ 8 (H-O/8)] + S

Problem 1

A coal sample has the following percentage composition:

C = 87%, H2 = 4.5%, O2 = 3%, S = 0.5%, moisture 3.5% and N2 = 0.5% and ash = 1%

Calculate the theoretical minimum weight of air required for the complete combustion of 1 kg of coal

Hint: Convert all % values of the elements into kg first

O2 req = 32/12*(870)+ 8*(45- (30/8)) + 5 in g = 2320+ 8*(41.25) +5 = 2320+ 330+5 = 2655g Air req = 100/23*2655 = 11,541 g Ans = 11.54 kg

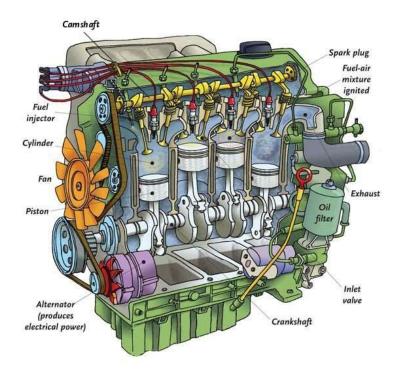
Problem 2

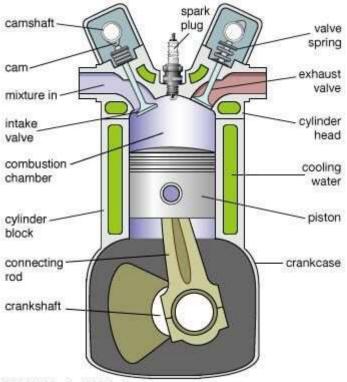
1 kg of a fuel oil has the following composition on analysis C = 90%, H = 6%, S = 2.5%, O2 = 1%, ash = 0.5%. Calculate the quantity of the air required for the complete combustion of 1kg of fuel by weight and by volume.

Calculate the minimum amount of air required for the complete combustion of 1m^3 of fuel containing the following composition by volume : CO = 20%, H₂ = 10%, CH₄ = 10%, CO₂ = 5%, N₂ = 50% and O₂ = 3%.

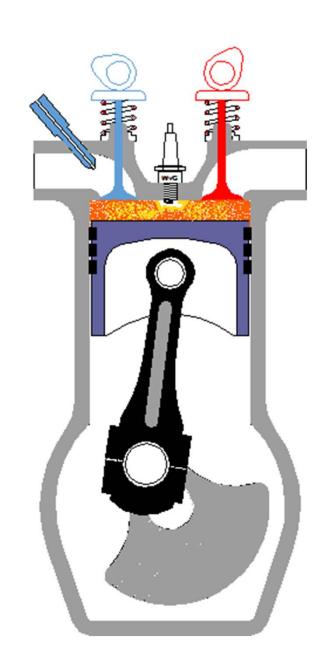
Knocking

- In an internal combustion engine, combustion of air/fuel mixture is initiated by the spark produced in the cylinder, which pushes the piston out
- 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 is known as **compression ratio**
- Good fuels give a high compression ratio, where uniform combustion takes place
- However, certain unwanted chemical constituents in the fuel cause non-uniform combustion,
 causing an explosive violence in side the cylinder which is known as knocking
- Compression ratio depends on the nature of constituents of the fuel. Efficiency of IC engine increases with compression ratio
- · The reason behind knocking characteristic of fuels are not fully understood





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COMBUSTION AND CAUSES OF KNOCKING

In a petrol engine, a mixture of gasoline vapor and air at 1:17 compression ratio is used as the fuel.

This mixture is compressed and ignited by an electric spark.

After the reaction is initiated by a spark, a flame should spread rapidly and smoothly through the gas mixture and the expanding gas drives the piston down the cylinder.

The products of oxidation reaction increases the pressure and pushes the piston down the cylinder.

The rate of oxidation of a hydrocarbon molecule depends on the number of carbon atoms in a molecule, structure and temperature.

If the combustion proceeds in a regular way, there is no problem in knocking. Compression ratio is defined as the ratio of the cylinder vol at the end of the suction stroke (V_2) to that at the end of the compression stroke (V_1) of the piston.

In some cases, the rate of combustion will not be uniform due to unwanted chemical constituents of gasoline or pockets of air-fuel mixture exploding in an uncontrolled manner during the suction stroke.

The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "Knocking".

Knocking property of the fuel reduce the efficiency of engine.

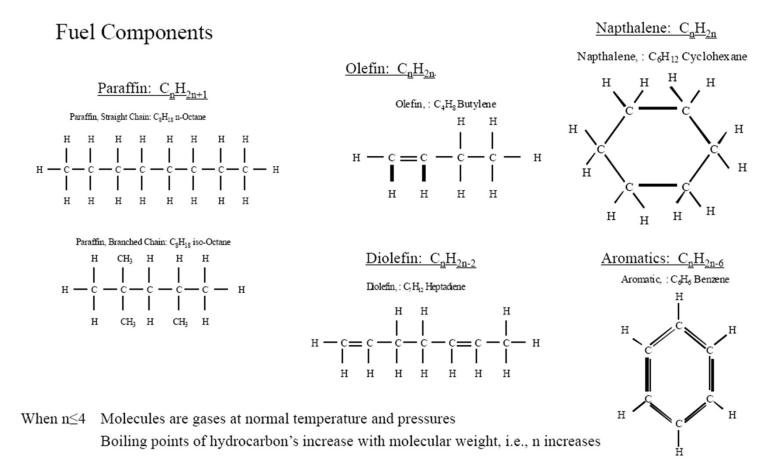
The tendency to knock depends not only on the fuel but also on the engine design, shape of head, location of plug, etc., and also upon the running conditions.

A good gasoline should resist knocking.

Hydrocarbons in different fuels

	<u>B.P</u>	C-atoms	<u>Uses</u>
Uncondensed gases	< 30°C	C ₁ -C ₄	LPG fuels
Gasoline/Petrol	40-120	C ₅ -C ₉	Fuel for IC engines
Naptha/S.Spirit	120-180	C ₉ -C ₁₀	Solvent in paints
Kerosene oil	180-250	C ₁₀ -C ₁₆	Fuel for stove & jet
Diesel oil	250-320	C ₁₅ -C ₁₈	Diesel engine fuels
Heavy oil	320-400	C ₁₇ -C ₃₀	Fuels for ships

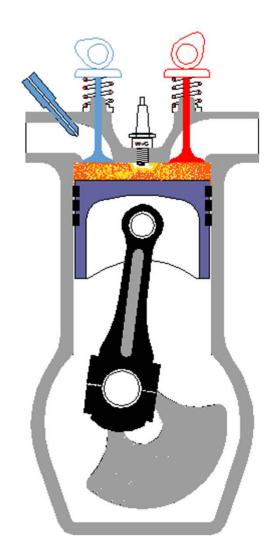
- Knocking tendency depends on the chemical structure of fuel, which decreases in the following order.
- Straight chain paraffins > Branched chain paraffins > Cycloparaffins > Olefins > Aromatics
- Knocking results in loss of efficiency of the engine
- Knocking characteristics of a combustion engine fuel (petrol) octane number or rating
- Antiknock quality of a fuel is expressed as its octane number



The knocking tendency decreases with increase in the compactness of the molecules, double bonds and cyclic structure.

Reason: Aromatic fuels such as benzol can be used at higher compression ratios without knocking than normal straight chain paraffinic petrol.

Straight chain HCs possess high vapour pressure (low b.p) than aromatics. Thus, the possibility for spontaneous ignition at higher compression is greater for straight chain hydrocarbons.



Octane number

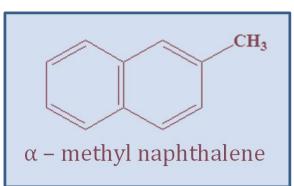
- Octane number gives the efficiency of fuel based on its knocking characteristics
- N-heptane was found to knock very badly and has been given an antiknock value of zero
- Iso-octane gives very little knocking and has been given an antiknock value of 100
- Octane number system has been devised between these two extreme numbers
- Octane number of a fuel is the percentage of iso-octane present in a mixture of iso-octane and n-heptane, which gives the same knocking characteristics of the fuel under test.
- E.g gasoline having 75 octane number is one having the same knocking characteristic as that of a 75:25 mixture of iso-octane and n-heptane

Fuel Additives to Reduce Knocking

- Chemical additives are used to raise the octane number of gasoline.
- The most effective antiknock agents are lead alkyls;
- (i) Tetraethyl lead (TEL), (C₂H₅)₄Pb was introduced in 1923
- (ii) Tetramethyl lead (TML), (CH₃)₄Pb was introduced in 1960
- Most effective antiknock agent is tetraethyl lead (TEL) along with ethylene dibromide which prevents deposition of lead by forming volatile lead halides
- Others are tetramethyl lead, tertiary butyl acetate, diethyl telluride
- About 1970 low-lead and unleaded gasoline were introduced over toxicological concerns with lead alkyls (TEL contains 64% by weight lead).
- Alcohols such as ethanol and methanol have high knock resistance.
- Since 1970 another alcohol methyl tertiary butyl ether (MTBE) has been added to gasoline to increase octane number.

Cetane number

- In diesel engines, the combustion of fuel is not by ignition as in petrol engines, but by the application of heat and pressure
- There is a delay period between the injection of diesel fuel and its ignition. If this
 delay period is large, too much fuel accumulates in the cylinder and burn very
 rapidly and causes diesel knock.
- Increasing delay period occurs in the series :
- n-paraffin < Olefins < naphthenes < isoparaffins < aromatics
- Order is the reverse for gasoline antiknock quality.
- n-hexadecane ; Cetane number = 100
- α methyl naphthalene; Cetane number = 0
- A given fuel matches in quality with the blend having 40/60 blend of cetane and methyl naphthalene, it is assigned a cetane number 40
- Cetane number of diesel can be improved by adding pre-ignition dopes such as amyl/butyl nitrite, carbamates, ditertiary butyl peroxide and metal organic compounds.



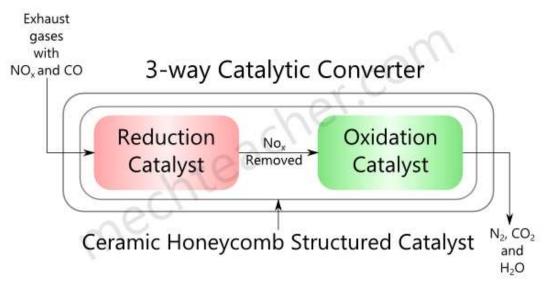
Three way catalytic convertor

- A 3-way catalytic converter is a sophisticated device used in the exhaust system of many modern petrol engine vehicles. It converts harmful gases in the engine exhaust to relatively harmless gases.
- The exhaust gases from an engine contain harmful substances such as oxides of nitrogen (NO_x) , carbon monoxide (CO) and Hydrocarbons (HC). These substances produce extreme environment hazards.
- 3-way catalytic converters convert these harmful substances to less harmful nitrogen (N_2) , carbon-di-oxide (CO_2) and water (H_2O) .

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

Reduction Catalyst and Oxidation Catalyst

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.



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 (NOx) to nitrogen (N2) and oxygen (O2). The following reactions take place when the exhaust gases pass over the reduction catalyst.

$$2NO \rightarrow N_2 + O_2$$

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

The reduction catalyst simply rips off nitrogen and oxygen from the oxides of nitrogen.

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) .

The following reactions takes place when the exhaust gases pass over the oxidation catalyst:

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

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

Note: The second reaction (above) is a generalized reaction. In it, HC stands for hydrocarbon. HC might be methane, ethane or other hydrocarbon.

The gases that finally come out of the catalyst chamber are N_2 , CO_2 , and H_2O . 3-way catalytic converters are so named because they are capable of eliminating three pollutants – NO_x , CO and HC.