Fuels and combustion

A fuel is defined as naturally occurring or artificially manufactured combustible carbonaceous material which serves particularly as source of heat and light and also in few cases as a source of raw material.

Classification of fuels:

1) Based on their origin fuels are classified into a two types.

a) Primary fuels b) Secondary fuels.

a) Primary Fuels: There are naturally occurring fuels which serves as source of energy without any chemical processing. Ex: Wood, Coal, Crude oil, Natural gas.

b) Secondary Fuels: They are derived from primary fuels & serves as source of energy only after subjecting to chemical processing. Ex: Charcoal, Coke, producer gas, Petrol, Diesel etc.,

2) Bases on their physical state fuel are classified into a) Solid b) Liquid c) Gaseous fuels.

Characteristics of a good fuel: A good fuel should satisfy the following requirements:

1) The fuel should have a high calorific value per unit weight i.e., it should evolve a large amount of heat when a unit weight of it is burnt under the conditions in which it is to be used as a fuel.

2) The moisture content should be low, so that its heating value should be high.

3) It should not produce harmful products like CO_2, SO_2, H_2S and other poisonous gases on burning, since they pollute the atmosphere.

4) A fuel should have low content of non-combustible matter in the form of ash or clinker. The presence of non- combustible matter will enhance the cost of storage, handling and disposal of the waste.

5) In case of solid fuel, the size should be uniform so that combustion is regular.

6) The combustion of the fuel should be controllable so that it can be started or stopped.

7) It should be economical and easily available.

8) An ideal fuel should have moderate ignition temperature. Normally low ignition temperature during storage and transport of fuel leads to fire hazards on the other hand, fuels with high ignition temperature is safe for storage, handling and transport.

SOLID FUELS:

The main solid fuels are wood, peat, lignite, coal and charcoal. In addition to these certain agricultural and industrial wastes such as rice husk, coconut and nut shells etc., are employed as fuels.

Coal:

Coal is a fossil fuel which occurs in layers in the earth's crust. It is formed by the partial decay of plant materials accumulated

millions of years ago and further altered by the action of heat and pressure.

Varieties of Coal: Coal is a natural fuel formed by the slow carbonization of vegetable matter buried under the earth some thousands of years ago. It is classified into four kinds based on the carbon content and the calorific value.

1) Peat 2) Lignite 3) Bituminous Coal 4) Anthracite Coal

1) Peat: It is the first stage of formation of coal from wood. It is brown, fibrous jelly-like mass. It contains 80-90% moisture. The composition of peat is C=57%; H=6%; O=35% Ash=2.5%. The calorific value of peat is 5400kcal/kg. It is a low−grade fuel due to high water content. It is used as a fertilizer and packing material.

2) Lignite: Lignite is immature form of coal. It contains 20-60% moisture. Air−dried Lignite contains C=60-70% O=20%. It burns with a long smoky flame. The calorific value of lignite is 6500-7100 kcal/kg. It is found in Palna of Rajasthan, Neveli to Tamil Nadu, Lakhimpur of Assam and Karewa of Jammu and Kashmir.

Uses: 1) It is used as a domestic fuel. 2) It is used as a boiler fuel for steam rising. 3) It is used in the manufacture of producer gas.

3) Bituminous Coal: It is a high quality fuel. Its moisture content is 4%. Its composition is C=83%, O=10%, H=5%and N=2%. Its calorific value is 8500 kcal/kg. Most of the bituminous coal is found in Jharkhand, Orissa, West Bengal, Chattisgarh and Madhya Pradesh.

Uses: 1) It is used in metallurgy. 2) It is used in steam raising. 3) It is used for making coal gas. 4) It is also used for domestic heating.

4) Anthracite Coal: It is the superior form of coal. it contains C=92-98%, O=3%, H=3% and N=0.7%. It burns without smoke. Its calorific value is 8700 kcal/kg. In India, it is found only in Jammu and Kashmir and that too in small quantity.

Uses: 1) It is used for steam raising and house hold purposes. 2) It is used for direct burning in boilers and in metallurgy. 3) It is used in thermal power plant. 4) It is used in coal tar distillation. 5) It is used in glass furnaces.

Analysis of coal: The composition of coal varies widely and hence it is necessary to analyze the coal samples so that the type of coal can be selected for a particular industrial use.

There are two methods: ultimate analysis and proximate analysis.

Proximate analysis: The proximate analysis determines the a) moisture, b) volatile matter, c) ash and d) fixed carbon percentages and analysis can be determined with a simple apparatus. It may be noted that proximate has no connection with the word "approximate".

a) Moisture content: Moisture is generally determined by heating a known quantity (1 g) of air-dried coal in a silica crucible to 105 ^{0}C to 110 ^{0}C for one hour in a hot air oven. After heating, the crucible is taken out and cooled in desiccator and weighed. The loss in weight is determined as the moisture content on percentage basis.

$$\% \text{ of moisture } = \frac{\text{loss in weight}}{\text{weight of coal sample taken}} \times 100$$

b) Volatile matter: The moisture free coal is taken in a silica crucible and heated for 7 minutes at temperatures of 925 ^{0}C ± 20 ^{0}C in a muffle furnace. The crucible is then taken out, cooled first in air and then in dessicator. The loss in weight is calculated as the volatile matter on percentage basis.

$$\% \text{ of volatile matter } = \frac{\text{loss in weight due to removal of volatile matter}}{\text{weight of coal sample taken}} \times 100$$

c) Ash Content: It is the weight of residue obtained after burning a weighed amount of dry coal in an open crucible at 700-750 ^{0}C for half an hour in a muffle furnace. The weight of the residue remaining in the crucible corresponds to the ash content of the coal. This is reported on percentage basis.

$$\% \text{ of ash } = \frac{\text{weight of ash formed}}{\text{weight of coal sample taken}} \times 100$$

d) Fixed Carbon: Fixed carbon represents the quantity of carbon in coal that can be burnt by a primary current of air drawn through the hot bed of fuel. The sum total of the percentages of moisture, volatile matter and ash subtracted from 100 gives the percentage of fixed carbon.

$$\% \text{ of fixed carbon } = 100 - (\% \text{ of moisture } + \% \text{ of volatile matter } + \% \text{ of ash})$$

Significance of proximate analysis:

Each constituent determined under proximate analysis has its own implication and importance in the assessment of the coal sample.

a) Moisture content: High percentage of moisture is undesirable because it increases the transport costs and reduces the calorific value. Also a considerable amount of heat is wasted in evaporating the moisture during combustion. Typical range is 0.5 to 10%

b) Volatile Matter: Volatile matters are the methane, hydrocarbons, hydrogen and carbon monoxide and non-combustible gases like carbon dioxide and nitrogen found in coal. The presence of non-combustible gases is always undesirable, since they do not add to the heat value. A high volatile matter containing coal gives long flames, high smoke and low calorific values. Hence, lesser the volatile matter better the rank of coal.

iii) Ash: Ash is formed due to the presence of non-combustible elements like Fe, Mn & Co. It is non-combustible, useless matter which is left behind when all the combustible matter have been burnt off from coal. Many Indian coals have high ash content. The nature of the ash and its amount in coal are vital in determining the quality of coal. Hence, lower the ash content, better the quality of coal. High ash content in coal normally leads to:
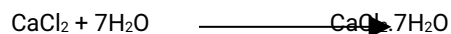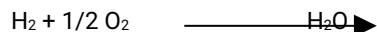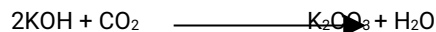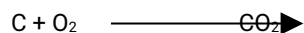
a)   Reducing the calorific value of coal.

b)   Causes the hindrance to the flow of air and heat, thereby decreasing the efficiency.

c)   Increases transporting, handling, storage and disposal costs.

d)   Ash if present as clinkers (lumps of ash) blocks the inter space of the grate, on which coal is burnt, thereby leading to irregular burning of coal and clinkers are bad conductors of heat and causes loss of fuel.

iv) Fixed Carbon: The percentage of fixed carbon helps in increasing the heating value of the fuel, because it is the fixed carbon that burns in the solid state. Higher the % of fixed carbon greater is the calorific value, smaller is the % of volatile matter and better the quality of coal. Therefore high % of fixed carbon in coal is desirable.

Ultimate analysis:

The ultimate analysis indicates the various elemental chemical constituents such as Carbon, Hydrogen, Oxygen, Sulphur, etc. The ultimate analysis is determined in a properly equipped laboratory by a skilled chemist.

i) Determination of carbon and hydrogen: A known weight of coal (1-2 gms) is burnt in a stream of pure oxygen in a combustion apparatus (fig.1). The carbon and hydrogen present in the sample are converted into CO_2, and H_2O, which are passed through two bulbs. One bulb containing weighed amount of anhydrous $CaCl_2$, absorbs H_2O and another bulb containing KOH absorbs CO_2.

$$C + O_2 \longrightarrow CO_2$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$H_2 + 1/2\ O_2 \longrightarrow H_2O$$

$$CaCl_2 + 7H_2O \longrightarrow CaCl_2.7H_2O$$

The weight of $CaCl_2$ and KOH in the bulbs are then determined. The increase in weight of $CaCl_2$ bulb represents the weight of H_2O formed, while the increase in the weight of KOH bulb represents the weight of CO_2 formed.

$$\% \text{ of carbon } = \frac{\text{increase in weight of KOH bulb}}{\text{weight of coal sample taken}} \times \frac{12}{44} \times 100$$

Where 12 represent the atomic weight of carbon and 44 represents the molecular weight of CO_2.

$$\% \text{ of hydrogen } = \frac{\text{increase in weight of CaCl2 bulb}}{\text{weight of coal sample taken}} \times \frac{2}{18} \times 100$$

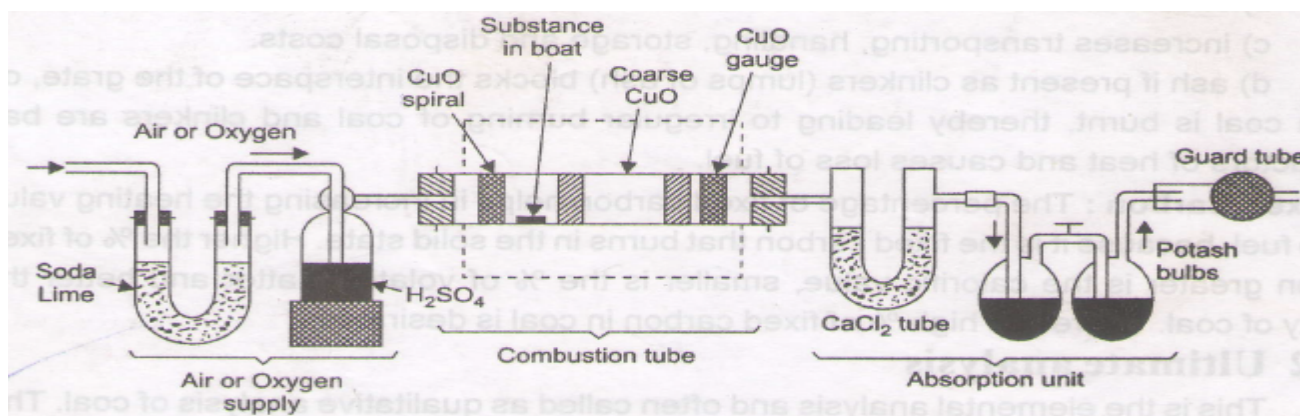Where 2 is the molecular weight of hydrogen and 18 is the molecular weight of H_2O.

Fig. 1. Carbon and hydrogen determination

ii) Determination of Nitrogen: Nitrogen in coal is determined by the Kjeldahl's method. 1 gm weight of powdered coal is heated with concentrated sulphuric acid along with K_2SO_4 and $CuSO_4$ in a long necked flask called Kjeldahl's flask, where K_2SO_4 and $CUSO_4$ are catalysts. After the solution becomes clear i.e., when whole nitrogen is converted into ammonium sulphate, it is treated with excess of NaOH to liberate ammonia. The liberated ammonia is distilled into a measured amount of standard acid. The volume of unused acid (H_2SO_4) is then determined by titrating against standard NaOH solution. Thus, the amount of acid neutralized by liberated ammonia is determined, from which the nitrogen present in the sample is calculated.

$$N_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 \uparrow$$
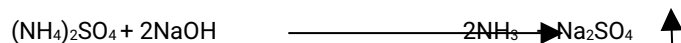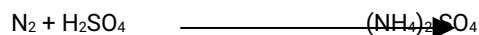
$$\% \text{ of nitrogen } = \frac{\text{volume of acid used } \times \text{normality of acid}}{\text{weight of coal sample taken}} \times \frac{14}{1000} \times 100$$

$$\% \text{ of nitrogen } = \frac{\text{volume of acid used } \times \text{normality of acid}}{\text{weight of coal sample taken}} \times 1.4$$

iii) Determination of Sulphur: This is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of calorific value. During this determination the sulphur is converted to sulphates. The washings are treated with barium chloride solution, when barium sulphate is precipitated. The precipitate of $BaSO_4$ is filtered, washed and dried.

$$\% \text{ of Sulphur } = \frac{\text{weight of BaSO4 (x)}}{\text{weight of coal sample taken}} \times \frac{32}{233} \times 100$$

Where 32 is the atomic weight of sulphur and 233 is the molecular weight of barium sulphate.

iv) Ash: determination is carried out as in proximate analysis.

v) Determination of Oxygen: It is determined by deducting the combined % of carbon, hydrogen, nitrogen and sulphur from 100.

$$\% \text{ of Oxygen } = 100 - [\% \text{ of } (C + H + N + S + Ash)]$$

Significance of ultimate analysis:

(a) Carbon and Hydrogen: The quality of coal is based on the percentage of carbon in it. Higher the percentage of better is the quality of coal and higher is its calorific value. The hydrogen no doubt is combustible but is usually present in combination with oxygen as water, which on being heated changes to steam. It is quite evident that calorific value of any fuel containing hydrogen, can only be due to hydrogen present in free state and not in combined form as water. So lesser the percentage of hydrogen the better the coal.

(b) Nitrogen: It has no calorific value and hence its presence in coal is undesirable.

(c) Sulphur: Though, sulphur increases the calorific value, its presence is undesirable because the combustion products SO_2 and SO_3 can corrode the equipment and also causes air pollution.

(d) Ash: Same as in proximate analysis.

(e) Oxygen: High oxygen content can reduce the calorific value of coal. 1% increase of oxygen content decreases the calorific value of coal by about 1.7%. Hence it is undesirable.

Liquid Fuels:

The thermal efficiency of liquid fuels is higher than solid fuels. Hence liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil called as primary fuel. Low boiling fractions of petroleum are used in internal combustion petrol engines and higher boiling fractions in internal combustion diesel engines and fired furnaces. A part of liquid fuels are also obtained synthetically from the hydrogenation of coal and water gas. Liquid fuels possess higher calorific value per unit mass than solid fuels.

Advantages:

1)   Liquid fuels are clean and require less amount of air for complete combustion.

2)   They possess higher calorific value than solid fuels.

3)   They are easy to transport through pipes.

4)   Due to cleanliness, loss of heat to chimney is low.

5)   Easily ignited and emission can be easily controlled.

6)   They are used as internal combustion fuels.

7)   They burn without forming dust, ash, etc.

Disadvantages:

1)   Care must be taken during storage.

2)   Cost is relatively higher than solid fuels.

3)   They give bad odour.

4)   Greater risk of fire hazards.

Petroleum or Crude Oil: The word 'petroleum'is derived from the Latin 'petra' (rock) and 'oleum' (oil). It is also known as crude oil or mineral oil. Petroleum is the main source of liquid fuels. Petroleum is a dark greenish-brown viscous liquid found in the earth's crust. The average composition of petroleum shows

C = 79.5 to 87.l% ; H = 11.5 to l4.8% ; S = 0.1 to 3.5% ; O+N = 0.1 to 0.5%

(i) Classification of Petroleum: According to chemical nature, petroleum is of three types:

(a) Paraffin-base petroleum composed of saturated hydrocarbons up to $C_{35}H_{72}$ which are semi-solids, called waxes.

(b) Asphaltic-base petroleum composed mainly of naphthalenes and cycloparaffins with smaller amounts of paraffins and aromatics.

(c) Mixed-base petroleum contains both the above type of compounds but is rich in semi-solid waxes.

Refining of Petroleum: petroleum obtained from the ground is a mixture of oil and unwanted impurities (water, dirt, sulphur compounds, etc). The process of removal of impurities from crude oil and separation of various fractions with different boiling ranges is called *refining of petroleum*. The plants set up for this purpose are called *oil refineries*. The whole process of refining of petroleum involves the following steps.

Step 1: Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged wherein the solids are removed.

Step 2: Separation of water (Cottrell's process): The crude oil is an emulsion of oil and salt water. It is allowed to flow through two

highly charged electrodes. The colloidal water droplets coalesce (join together or integrate) to form large drops which separate out from the oil.

Step 3: Removal of sulphur compounds: Sulphur compounds have objectionable properties of pollution. When the crude oil is treated with copper oxide, a reaction occurs with sulphur compounds which results in the formation of copper sulphide precipitate, which is then removed by filtration.

Step 4: Fractional distillation: The crude oil is then subjected to about 400 ^{0}C temperature in an iron retort. All volatile constituents are evaporated. The constituents, tar and asphalt, do not vapourise and they settle at the bottom of the retort. The hot vapours are then passed through a fractionating column.

Fractionating column is a tall cylindrical tower containing a number of horizontal stainless steel trays at a short distance. Each tray is provided with a small chimney, covered with a loose cap. As the vapours go up, they begin to cool and fractional condensation takes place at different levels of column (Fig. 2). Higher boiling fractions condense first while lower boiling fractions condense next. Thus the crude oil is fractioned into different fractions depending upon their boiling ranges.
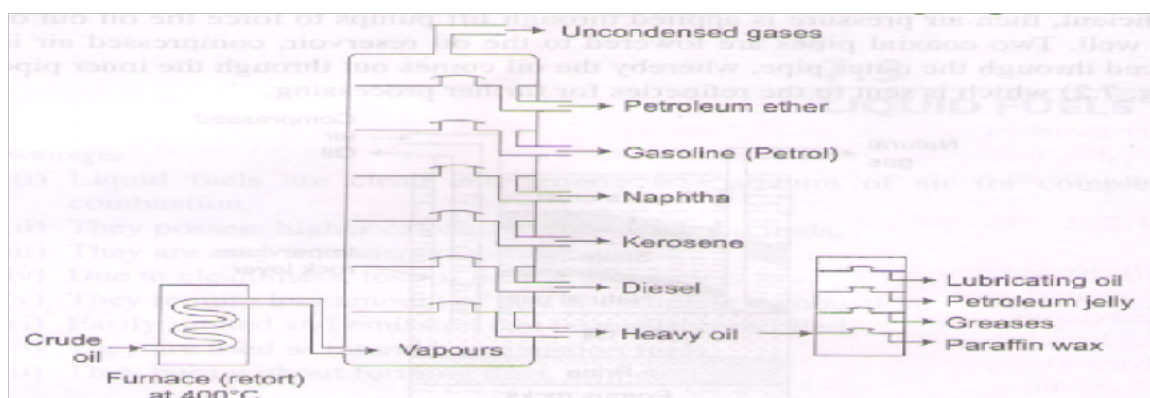

Fig. 2. Refining of petroleum using a fractionating column

Fraction	Boiling range	Composition	Uses
Uncondensed gas	Below 30°C	$C_1 - C_4$	As domestic or industrial fuel (LPG)
Petroleum ether	30°C – 70°C	$C_3 - C_7$	As a solvent
Gasoline or petrol	40°C – 120°C	$C_5 - C_9$	As a motor fuel, solvent and in dry cleaning
Naphtha	120°C – 180°C	$C_9 - C_{10}$	As a solvent and in dry cleaning
Kerosene oil	180°C – 250°C	$C_{10} - C_{16}$	As an illuminant, fuel for stoves
Diesel oil	250°C – 320°C	$C_{15} - C_{18}$	As a fuel for diesel engines
Heavy oil	320°C – 400°C	$C_{17} - C_{30}$	For setting gasoline by cracking process
This on refractionation gives			
(a) Lubricating oil			As lubricant
(b) Petroleum jelly			Used in cosmetics and medicines
(c) Grease			As lubricant
(d) Paraffin wax			In candles, boot polishes, wax paper

Important Petroleum Products and their Uses:

(a) Gasoline or petrol: It is obtained between 40-120 ^{0}C and is a mixture of hydrocarbons such as C_5H_{12} to C_9H_{20}. Approximate composition is C = 84%. H= 15%, N + S + O = 1%. Its calorific value is 11,250 K.cal/kg and is used as a fuel for internal combustion

engines of automobiles.

(b) Kerosene oil: It is obtained between 180-250 ^{0}C and is a mixture of hydrocarbons such as $C_{10}H_{12}$ to $C_{16}H_{34}$. Approximate composition is C = 84%, H = 16%, S = less than O.1%. Its calorific value is 11,100 K.cal/kg and used as fuel in jet engine and for making oil gas.

(c) Diesel oil: It is a fraction obtained between 250-320 ^{0}C and is a mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbons. Its calorific value is 11,000 K.cal/kg and is used as a diesel engine fuel.

CRACKING:

Among the fractions obtained by distillation of crude oil, the gasoline fraction (also termed as straight run petrol) is of demand as a motor fuel due to increased popularity in the automobile industry. This enhanced demand cannot be met from simple distillation of crude oil which yields gasoline of not such good quality. This difficulty was resolved by a process of thermal decomposition known as *cracking*. The objective of cracking is to obtain greater yields of improved gasoline by thermal decomposition of heavier fractions.

Thus cracking can be defined *as the process, by which the higher hydrocarbons (having high molecular weights) are decomposed into lower hydrocarbons by the application of heat.*

For example $C_{10}H_{22}$ (higher saturated hydrocarbon) cracks giving rise to paraffinic and olefinic hydrocarbons i.e.,

$$C_{10}H_{22} \xrightarrow{\text{Cracking}} C_5H_{12} + C_4H_8$$
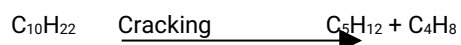
These simpler molecules will decompose further to the end products C and H under different conditions i.e.,

$$CH_4 \xrightarrow{\hspace{2cm}} C + 2H_2$$

There are two methods of cracking. They are a) Thermal cracking b) Catalytic cracking

Thermal cracking: In this method the heavy oil is subjected to high temperature and pressure where the higher hydrocarbons get converted into the lower hydrocarbons. The liquid after being cracked passes through the fractionating column and gets separated into different fractions. The yields are generally from 7 to 30%. Thermal cracking can carried out in two ways. They are   i) Liquid phase cracking and ii) Vapour phase cracking.

1) Liquid phase thermal cracking: The heavy oil or the gas oil stock is maintained at a temperature of 420-550 ^{0}C and under high pressure of 100 kg/cm^2 so that the reaction product is kept in the liquid state. By this method any type of the fuel, solid or liquid can be cracked. The yield obtained over here is 60-65% and the octane rating of the product is 65 to 70.

2) Vapour phase thermal cracking: In this process, the heavy oil is first vaporized by heating to about 600 ^{0}C and maintaining low pressures of 4-10kg/cm^2. Only oils of high volatility are suitable for this process and the yield is about 70%. Even though the products obtained by this process are associated with better anti-knocking properties and its stability is low when compared to liquid phase cracking.

Catalytic cracking: A better quality and yield is obtained by the process of catalytic cracking than the thermal cracking. The liquid is cracked at a temperature of 400-450 ^{0}C in the presence of a catalyst. Usually aluminium silicates [$Al_2(SiO_3)_3$] or alumina [Al_2O_3] are employed as catalysts. The catalytic cracking possesses some advantages over thermal cracking. They are

1)   The yield of the gasoline is higher.

2) The quality of the gasoline produced is better.

3) No external fuel is necessary for burning. The heat required for burning is derived from the coal embedded in the catalyst, during regeneration process.

4) Requirement of low pressure for cracking.

5) The process can be easily controlled during cracking and so the desired products can be obtained.

6) The product obtained after cracking contains a very little amount of S, a major portion of which escapes out as H_2S.

7) The product of cracking contains a high amount of aromatics.

8) The gasoline produced has a higher octane rating.

There are two methods of catalytic cracking. They are (i) Fixed bed catalytic cracking and (ii) Fluid bed catalytic cracking.

Fixed bed catalytic cracking: In this process, the oil is preheated to vapour in a preheater maintaining a temperature of 425 ^{0}C-450 ^{0}C and then passed through the catalytic chamber containing the catalyst (containing artificial clay mixed with zirconium oxide) maintained at 425-450 ^{0}C and 1.5 kg/cm^2 pressure. About 40% of heavy oil is converted into gasoline and about 2-4% carbon is formed. The latter gets absorbed on the catalyst bed. The vapours are then passed through the cooler where gasoline condenses along with some gases and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer where the dissolved gases are removed and pure gasoline is recovered (Fig. 3).

Note: The catalyst, after 8-10 hours stops functioning, due to deposition of carbon. This is reactivated by burning off the deposited carbon.
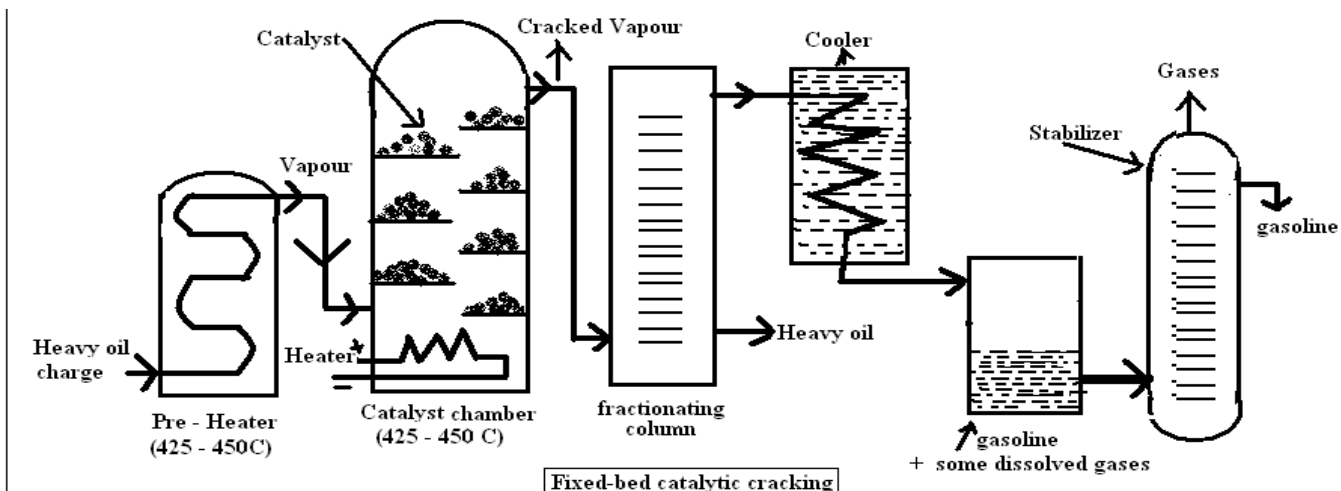

Fig. 3. Fixed-bed catalytic cracking

Knocking of petrol engines:

In a properly functioning engine, the compressed air-fuel mixture burns with the flame front progressing smoothly from the point of ignition across the combustion chamber. However, at high compression ratios, depending on the composition of the fuel, some of the air-fuel mixture may spontaneously ignite ahead of the flame front and burn in an uncontrolled manner, producing intense high-frequency pressure waves. These pressure waves force parts of the engine to vibrate, which produces a rattling sound and is called as

knocking.

The knocking can be defined as the rattling sound produced in a petrol engine caused by premature combustion of part of the compressed air-fuel mixture in the cylinder.

Knocking causes loss of efficiency of the engine, increases fuel consumption and damages the spark plug.

The chemical structure of the petrol is responsible for knocking. The following is the order of the constituents responsible for knocking.

Strait chain paraffins > branched-chain paraffins > Olefins > cyclo-paraffins (naphthalenes) > aromatics.

Thus, olefins of the same carbon chain length possess better anti-knock properties than the corresponding paraffins and so on.

Octane rating: The extent of knocking of petrol is measured by a test called **octane rate or octane number**.

Octane rating is introduced by **Edger** in 1872. It has been found that n-heptane knocks very badly and hence, its anti-knock value has arbitrarily assigned as Zero. On the other hand, isooctane (2,2,4-trimethylpentane) produces very little knocking, so its anti-knocking value has been given as 100.

Thus several mixtures of n-heptane and isooctane were prepared like isooctane:n-heptane-40:60, 60:40, 70:30 etc. Each mixture is taken into an internal combustion engine and its knocking characteristic is measured and matched with the knocking characteristic of petrol sample under examination. For example, octane number of the petrol test sample matches with 70:30 mixtures, the octane number of the test sample is 70.

The octane number can be defined as the percentage of isooctane in a mixture of isooctane and n-heptane whose knocking characteristic matches with the knocking characteristic of the petrol sample under examination.

Improving the anti-knocking property of petrol: The octane number of anti-knocking property of petrol can be improved by adding the anti-knocking agents such as tetra ethyl lead, $(C_2H_5)_4Pb$ or TEL and diethyl telluride, $(C_2H_5)_2Te$. In motor spirit (or motor fuel), about 0.5 ml and in aviation fuel about 1.0 to 1.5 ml of TEL is added per liter of petrol. But these are poisonous materials. Another disadvantage of TEL is the peroxide formed is deposited on inner walls of the IC engine, which is harmful. To eliminate these peroxides, ethylene dibromide is added which converts the lead peroxide to volatile lead bromide which escapes out along with other flue gases. However, lead bromide is harmful to the environment.

Alternative method of increasing octane number of fuel is by adding alternative anti-knocking agents like isopropyl benzene and methyl tertiary butyl ether (MTBE).

Diesel:

Diesel or gas oil is a fraction obtained between 250-320 ^{0}C during fractional distillation of petroleum. This oil contains 85% of carbon, 12% of hydrogen and calorific value is 11,000 Kcal/mole. Diesel is an important fuel for automobiles.

Knocking of Diesel:

Diesel knock can be defined as the rattling sound produced in the engine due to ignition-lag or the delay in the ignition of the fuel.

The structure of diesel is responsible for the knocking. The order of anti-knocking property of hydrocarbon constituents of

diesel fuel is as follows.

n-alkenes > naphthalenes > alkenes > branched alkanes > aromatics.

Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.

The extent of diesel knock is measured by **Cetane number.** For this hexadecane is a straight chain hydrocarbon selected which is having 100 % anti-knocking property. 2-methylnaphthalene is an aromatic compound whose anti diesel knocking property is zero.

The cetane number can be defined as the percentage of cetane in a mixture of cetane and 2-methylnaphthalene whose diesel knocking characteristics matches with the anti-knocking property of diesel fuel sample under examination.

Gaseous fuels:

The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition. Like the other two types of the fuels the gaseous fuels can also be classified into two types.

a) Primary fuels e.g. Natural gas

b) Secondary fuels e.g. coal gas, producer gas, water gas, carburetted water gas, oil gas, blast furnace gas etc.

Advantages of gaseous fuels:

1) Their combustion can easily be controlled.

2) They possess high calorific value.

3) They easily transport through pipe lines.

4) They require less amount of air for complete combustion

5) They are free from solid and liquid impurities.

6) They are easy to ignite.

7) They burn without smoke and produce no ash.

Disadvantages:

(i) They are highly inflammable. (ii) They require very large storage tanks.

(iii) They are costlier than solid and liquid fuels.

Natural gas: The natural gas is obtained from the wells dug in the earth during mining of petroleum. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons. If the lower hydrocarbons are present the gas is called dry gas or lean gas, but if the hydrocarbons having the higher molecular weights are present the gas is known as rich gas or wet gas. It is also known by the name of marsh gas as a major portion of it is contributed by methane. The average composition of naiural gas is as follows.

Methane (CH_4)- 88,5%; Ethane (C_2H_6) - 5.5%; Propane (C_3H_8) -3.7%; Butane C_4H_{10}- 1.8%

Pentane, H_2, CO, CO_2, and higher hydrocarbons - 0.5%

The calorific value of natural gas varies from 8000-14000 k.cal/m^3. Natural gas is subjected to various treatments before it reaches the consumer. For e.g. Natural gas contains appreciable quantities of H_2S which can be removed by scrubbing with

monoethanolamine.

Natural gas is an excellent domestic fuel which can be carried to long distances in pipelines as town gas in U.S., U.K and Mumbai highway and also as an industrial fuel. It is also used for manufacturing a number of chemicals like carbon black, methanol, formaldehyde etc. Methane on microbiological fermentation gives synthetic proteins which are used as animal feed. It is also used for generation of electricity in fuel cells. Natural gas is also used as a source of H_2. Hence, ammonia can be made by reacting N_2 with H_2 obtained from natural gas.

LPG (Liquified Petroleum Gas or Bottled Gas or Refinery Gas): LPG is obtained as a byproduct during the cracking of heavy oil or from natural gas. LPG is dehydrated and desulphurised. It is supplied under pressure in containers after treating the LPG with mercaptans to detect the leakage of gas. LPG is supplied under different trade names like Indane, H.P etc. LPG is a highly volatile, colourless liquid under pressure. LPG is highly inflammable and consists of hydrocarbons that can be readily liquified under pressure and exist as gas at atmospheric pressure. The composition of LPG is n-butane, isobutane, butylene and propane. The calorific value is 27,800 Kcal/m^3 and LPG is knock resistant and burns cleanly with little residue or contamination. It increases the engine life.

Uses:

1. The largest use is as domestic fuel.

2. This is also used widely as an industrial fuel.

3. LPG is used as a fuel in certain class of vehicles like trucks and tractors.

4. LPG leaded with (TML) Tetetramethyl lead can be used as fuel for the railway diesel locomotives.

5. It is advantageously used in engines working under high compression ratio.

Disadvantages: Handling has to be done extreme carefully to avoid accidental hazards.

Compressed Natural Gas (CNG): CNG is produced by pressing natural gas to a high pressure of about 1000 atmospheres. It is now used as a substitute for petrol and diesel. The main component present in it is methane. CNG is the cheapest and cleanest fuel. Ignition temperature of CNG is 55 ^{0}C. However, initial cost of engine designed to use CNG as a fuel is comparatively higher than that of engine designed to use petrol or diesel.

Advantages of CNG as motor fuel:

(a) The operating cost of CNG fuel is much lower compared to gasoline operation.

(b) Combustion of CNG leads to lesser CO emission than gasoline

(c) It mixes better with air than liquid fuels

(d) It is a much safer fuel, since it ignites at a higher temperature than gasoline and diesel.

(e) It is a much less pollution causing fuel.

Combustion

Combustion is a process of combination of an element with oxygen by liberation of heat. It is an exothermic reaction.

For example. $C_{(s)} + O_2$ ⎯⎯→ $CO_2 - \Delta H$ 97 Kcal.

For combustion of a fuel, it should be brought to its kindling or ignition temperature. *The combustion may be defined as the minimum temperature at which the substance ignites and burns without further addition of heat from outside.*

The combustible elements in a fuel are C, H & S and produce CO, CO_2, H_2O and SO_2 respectively. The extent of combustion and the efficiency of a fuel are determined by the analysis of gases coming out of exhaust, which is called *flue gas*. The flue gas contains CO_2, CO, H_2O, O_2 and N_2 as its constituents.

Problems on Combustion: Combustion is an exothermic chemical reaction accompanied by the development of heat. e.g. combustion of carbon in oxygen is represented as

$$C_{(s)} + O_2 \longrightarrow CO_2 + 97 \text{ Kcal.}$$
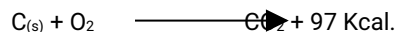
It is defined *"as the process of oxidation of the fuel by oxygen and subsequent liberation of energies like heat, light etc".* All the fuels contain carbon which contributes the major portion of heat evolved. Sulphur and hydrogen too get oxidized to sulphur dioxide and water but the heat produced is unimportant due to it being small (because the sulphur and hydrogen are present to little extent). The air which is mostly employed for the combustion of the fuels contain 21% of oxygen by volume and 23% of oxygen by weight, the remaining being nitrogen.

The gaseous products of combustion are mainly CO, CO_2, N_2, O_2, SO_2, and H_2O which are known as flue gases. While studying the combustion of fuels C, H, S, CO and hydrocarbons should be considered for complete oxidation in excess of air.

Calculations on combustion: To find the amount of oxygen and hence the amount of air required for the complete combustion of a unit quantity of fuel, it is necessary to apply some elementary principles as outlined below.

a) Substance always combines in definite proportions and these proportions are determined by the molecular masses of the substances involved and the products formed

example: $C_{(s)} + O_2 \qquad CO_2$

Mass proportions   12   32   44
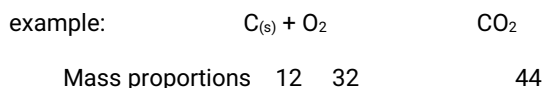
This equation indicates that mass proportions of carbon, oxygen and carbon dioxide formed are 12 : 32 : 44.

b) 22.4 litres of any gas at STP (0^0C and 760 mm of Hg pressure) has a mass equal to its mole.

c) Air contains 21% of O_2 by volume and mass percent of O_2 is 23. This means that 1 Kg of O_2 is supplied

by $\dfrac{1 \times 100}{23}$ =4.35 kg of air

Similarly, 1 m^3 of O_2 is supplied by $\dfrac{1 \times 100}{21}$ =4.76 m^3 of air

d) Molecular mass of air is taken as 28.94 g/mol.

e) Minimum O_2 required = Theoretical O_2 required − O_2 present in the fuel.

f) Minimum O_2 required should be calculated on the basis of complete combustion the combustion. If the products contain CO and O_2 then excess of O_2 is found by subtracting the amount of O_2 required burning CO to CO_2.

g) The mass of the dry flue gases formed should be calculated by not consisting H_2O in products of combustion.

a) Combustion of carbon:

$$C_{(s)} + O_2 \longrightarrow CO_2$$
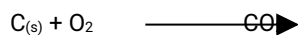
Mass proportions   12   32   44

12 kg of carbon requires 32kg of oxygen for complete combustion. Therefore the amount of oxygen required for complete combustion of x kg of carbon is given as $\dfrac{x \times 32}{12} kg$

b) Combustion of hydrogen:

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O$$
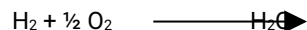
2   16   18

2 kg of hydrogen requires 16 kgs of oxygen for complete combustion. Therefore the amount of oxygen required for complete combustion of y kg of hydrogen is given as $\dfrac{y \times 16}{2} kg$

It may b pointed out here that of the total amount of hydrogen, some of it is present in combined form i.e. as H_2O. As this combined hydrogen is a non combustible substance, it does not take part in combustion.

Now 1 part of hydrogen combines chemically with 8 parts by mass of oxygen, the amount of hydrogen available for combustion $= \text{mass of hydrogen} - \dfrac{\text{mass of oxygen}}{8} = \left(H - \dfrac{O_2}{8} \right)$

Hence the oxygen required for combustion of hydrogen $= \dfrac{16}{2}\left(H - \dfrac{O_2}{8} \right) = 8\left(H - \dfrac{O_2}{8} \right)$

c) Combustion of Sulphur:

$$S + O_2 \longrightarrow SO_2$$

32   32   64

32 kgs of sulphur requires 32 kgs of oxygen for complete combustion. Therefore the amount of oxygen required for complete combustion of S kg of sulphur is given as $\dfrac{32}{32} \times S \ kg$

On combining the above three combustion equations we get the equation for the theoretical oxygen requirement for the combustion of C, H and S as $= \dfrac{32}{12} C + 8\left(H - \dfrac{O_2}{8} \right) + S$

Where C, H, S and O_2 represent the masses of carbon, hydrogen, sulphur and oxygen respectively per kg of the fuel.

Since the percentage by weight and volume of oxygen in air is 23 and 21, the amount of air required theoretically for combustion of I kg of fuel is given as

Minimum weight of air required for combustion $\dfrac{100}{23}\left[\dfrac{32}{12} C + 8\left(H - \dfrac{O_2}{8} \right) + S \right] kg$

For calculating the volume of air required, *the weight of O₂ required for combustion must be converted to volume of O₂* and then calculated as

$$= \frac{\text{volume of oxygen required for combustion} \times 100}{21} \text{ litres}$$

Points to be followed for solving problems on combustion:

While calculating the problems on combustion the following points should be followed in the given order.

1. The first step in combustion problems is to convert percentage composition into actual composition.

2. Wt. of oxygen should be calculated.

3. Wt. of oxygen should be converted to volume of oxygen.

4. Wt. of air required then volume of air required must be calculated.

5. Products of combustion by weight and then percentage composition by weight must be calculated.

6. Products of combustion by volume and then percentage composition by volume must be calculated.

7. The important formulas to be remembered are (1) one gram mole of any substance occupies a volume of 22.4 liters. (2) 100 parts by weight of air contains 23 parts of O_2 (3) 100 parts by volume of air contains 21 parts by volume of O_2 and 79 parts of N_2.

Calorific value:

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its **calorific value**.

The calorific value of a fuel can be defined as *"the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen".* There are different units for measuring the quantity of heat. They are:

1. **Calorie:** It is the amount of heat required to increase the temperature of 1 gm of water through one degree centigrade.

2. **Kilocalorie:** This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade. 1 k.cal = 1000 cal

3. **British thermal unit (B.Th.U.):** This is the unit of heat in English system. It is defined as "the quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit. 1 B.Th.U = 252 cal = 0.252 k.cal

4. **Centigrade heat unit (C.H.U.):** It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade. 1 k.cal = 3.968 B.Th.U. = 2.2 C.H.U.

Generally a fuel is evaluated from its total calorific value i.e. higher calorific value (HCV) and lower calorific value (LCV) (net calorific value).

Inter conversion of various units of heat:

On the basis that 1 kg = 2.2lb and 1 ^{0}C = 1 .8 ^{0}F we have

1 k.cal = 1000 cal = 3.968 B.Th. U. = 2.2 C.H.U. and 1 B.Th.U = 252 cal

Units of calorific value:

For solid or liquid fuels : cal/g or k.cal/kg, B.Th.U/lb.

For gaseous fuels . k.cal/cubic meter (k.cal/m3) and B.Th.U./ft^3 i e. B.Th.U /cubic feet

Relation between various units:

1 k.cal/kg = 1.8 B.Th.U/lb = 1 cal/g

1 k.cal/m^3 = 0.1077 B.Th.U/ft^3

1 B.Th.U/ft^3 = 9.3 k.cal/m^3

Higher or Gross calorific value (GCV): Usually all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen gets converted to steam. If the products of combustion are condensed to the room temperature, the latent heat of condensation of steam also gets included in the measured heat, which is then called *"higher or gross calorific value".* Therefore the higher calorific value is defined as *the total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to 60^{0}F or 15^{0}C (room temperature).*

Lower calorific value or Net calorific value (NCV): Whenever a fuel is subjected to combustion, the water vapour and moisture etc., escape along with the hot combustion gases and hence there is no chance for their condensation. So the net or lower calorific value (LCV) is defined as *"the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape".*

LCV = HCV - Latent heat of water vapour formed.

Since 1 part by mass of hydrogen produces 9 parts by mass of water as given by the equation below

H$_2$ + ½ O$_2$ ———————— H$_2$O ▶

2g   18g

1g   9g
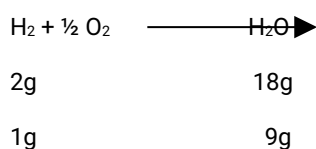
Hence LCV = HCV - mass of hydrogen x 9 x latent heat of steam.

The latent heat of steam is 587 k.cal/kg or 1060 B.Th.U./lb of water vapour formed at room temperature. In other words

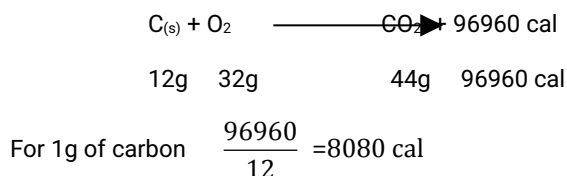$$\text{Net C.V} = \text{gross C.V} - 9 \times \frac{H}{100} \times 587$$

$$= \text{gross C.V.} - 0.09 \times H \times 587$$

Where H=% of hydrogen in the fuel
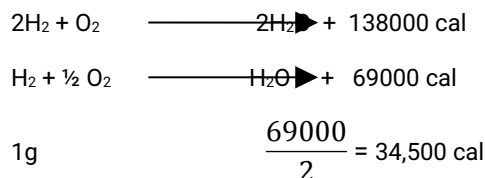
Theoretical calculation of calorific value:

The calorific value of a fuel can approximately calculated by noting the amount of the components constituting the fuel. In such cases we take into consideration the heat of the reaction which is defined as "the amount of heat produced when one gram molecule of the reactants is burnt in the presence of oxygen. For e.g

$$C_{(s)} + O_2 \longrightarrow CO_2 + 96960 \text{ cal}$$

$$12g \quad 32g \qquad\qquad 44g \quad 96960 \text{ cal}$$

For 1g of carbon $\dfrac{96960}{12}$ =8080 cal

So one gram of carbon gives 8080 cal of heat.

Similarly H_2 burns in the presence of O_2 resulting the formation of water.

$$2H_2 + O_2 \longrightarrow 2H_2O + 138000 \text{ cal}$$

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O + 69000 \text{ cal}$$

$$1g \qquad\qquad \dfrac{69000}{2} = 34,500 \text{ cal}$$

So 1 gm of hydrogen when burnt into water gives 34,500 calories of heat. The end products of the fuels mostly happen to be water and carbon dioxide. Hence with knowledge of their heats of combustion, we can approximately find the calorific value of any fuel containing them. But in case of other fuels which may contain O, S and halogens it is not possible to compute their calorific value so easily. Many formulae have therefore been put forward from time to time to calculate the calorific value of fuels.

Dulong Formula: In this formula the higher calorific value (HCV) of a fuel is the total of the calorific value of each of the components. Secondly 8 parts by weight of O_2 combine with one part by weight of hydrogen. So if oxygen is present, it must be present in the combined form with hydrogen as water thereby decreasing the amount of hydrogen available for combustion by O/8. The formula is then

$$GVV \text{ or } HCV = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O_2}{8}\right) + 2240 \times S\right] cal/g$$

Where C, H, O, S are the percentages of carbon, hydrogen, oxygen and sulphur respectively, as determined by the ultimate analysis of fuels. The calorific values of the components of fuels are out lined below:

Constituent	Calorific value (Kcal/kg)
Hydrogen	34,500
Carbon	8080
Sulphur	2240

Solved examples based on calorific value:

Problem: Calculate the gross and net calorific value of a coal sample having the following composition C=8-%, H=7%, O=3%, S= 3.5%, N = 2% and ash=5%.

Solution:

$$GCV = \frac{1}{100}\left[8080 \, C + 34500\left(H - \frac{O_2}{8}\right) + 2240 \, S\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right] = 8828 \text{ kcal/kg}$$

And NCV=GCV-0.09 H x 587 = 8828 - 0.09 x 7 x 587 = 8458 kcal/kg

Experimenial determnation of calorific value: The calorific value of a fuel is determined by the combustion of the fuel in a special type of the apparatus called calorimeter. The different types of calorimeters are

1) The Bomb calorimeter 2) The Boy's calorimeter and 3) The Junker's calorimeter

The bomb calorimeter is used in finding the calorific value of solid and liquid fuels. The Boy's calorimeter is used for determining the calorific values of gaseous fuels and those liquid fuels which are easily vapourized.