Fuels and Combustion

INTRODUCTION

- **Fuels**

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives large amount of heat that can be used economically for domestic and industrial purposes. During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc combine with oxygen with simultaneous liberation of heat. The calorific value of a fuel depends mainly on the two elements.

$$C + O2 \longrightarrow CO2 \quad + \; 94 \text{ kcals.}$$

$$2H2 + O2 \longrightarrow 2H2\,O \quad + \; 68.5 \text{ kcals.}$$

Classification of Fuels

- 1. **Primary fuels** which occur in nature as such, e.g. coal, petroleum and natural gas.
- 2. **Secondary fuels** which are **derived from the primary fuels**, e.g. coke, gasoline, coal gas, etc.
- Both primary and secondary fuels may be further classified based upon their physical state as
- (i) solid fuels (ii) liquid fuels and (iii) gaseous fuels.

CALORIFIC VALUE

- Calorific value of a fuel is "**the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely**."

Units of heat :

(1) **'Calorie'** is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).

(2) "**Kilocalorie**" is equal to 1,000 calories. It 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 = 1,000 cal**

(3) "**British Thermal unit" (B.T.U.)** is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.

1 B.T.U. = 252 cal = 0.252 kcal   1 kcal = 3.968 B.T.U.

HCV and LCV

Higher or gross calorific value(HCV or GCV):

- Usually, all fuels contain some hydrogen and hydrogen is converted into steam. If the products of combustion are condensed to the 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 calorific value
- ". So, gross or higher calorific value (HCV) is "the total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature"(i.e., 15°C or 60°F).

Lower or net calorific value (LCV or NCV)

- **In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along-with hot combustion gases. Hence, a lesser amount of heat is available. So, net or lower calorific value (LCV) is "the net heat produced, when unit mass /volume of the fuel is burnt completely and the products are permitted to escape".**
- **Net calorific value= Gross calorific value - Latent heat of condensation of water vapour produced**

- $1/2H_2 + O_2 \xrightarrow{\qquad} H_2O$

2g 16g 18g

1 8 9

NCV = GCV - Mass of hydrogen per unit weight of the fuel burnt x 9 x Latent heat of condensation of water vapour that is equal to 587 kcal/kg.

(This is based on the fact that 1 part of H by mass gives 9 parts of H_2O, and latent heat of steam is 587 kcal/kg)

If the percentage (%) of Hydrogen (H) is given

LCV = [HCV - 9H/100 x 587] kcal/kg

= [HCV - 0.09 H x 587] kcal/kg

- **Dulong's formula** for calorific value from the chemical composition of fuel is :

- HCV = 1/100 [8,080 C + 34,500 (H – O/8)+ 2,240 S] kcal/kg

- where C, H, O, and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water, and

- LCV = [HCV - 9H/100 x 587] kcal/kg = [HCV - 0.09 H x 587] kcal/kg

Solid fuel

COAL

- Coal is regarded as a fossil fuel produced from large accumulations of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years. Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions. It is chiefly composed of C, H, N, and 0, besides non-combustible inorganic matter.

Classification of Coal

- Coals are classified on the basis of their rank. Rank is defined as the degree or extent of maturation and is therefore a qualitative measure of carbon contents. Peat, lignite and sub-bituminous coals are referred as low rank coals while bituminous coals and anthracites are classed as high rank. In European terminology, the lignite and sub-bituminous coals are called soft coals while bituminous coals and anthracite coals are termed as hard coals. In North American terminology, the coal series is written as
- **Wood peat lignite bituminous**

  anthracite.

Analysis of Coal

- In order to assess the quality of coal the following two types of analysis are made.

- **1. Proximate Analysis** It includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.

- **2. Ultimate Analysis** It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. Since it is used
- For the determination of elements present in the coal, it is also called elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong's formula.

Proximate analysis

- (1) **Moisture**: About 1 g of finely powered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105° - 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).
- $$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$
- (2) **Volatile matter**: The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at 925°± 20°C. The crucible is taken out of the oven after 7 *minutes* of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

Percentage of volatile matter=

$$\frac{\text{Loss in weight due to removal of volatile matter}}{\text{Wt. of coal sample taken}} \times 100$$

- (3) **Ash:** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at 700 ± 50° C for 1/2 *hour*. The crucible is then taken out, cooled first in air, then in desiccator and weighed.

- Heating, cooling and weighing is repeated, till a *constant weight* is obtained. The residue is reported as ash on percentage-basis.

- $$\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$$

(4) **Fixed carbon**: Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash)

- high percentage of rued carbon is desirable.

Importance of proximate analysis

- Proximate analysis provides following valuable informations in assessing the *quality of coal:*

- **(1) Moisture:** Moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".

- **(2) Volatile matter**: A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal. Higher volatile content in coal is undesirable.

- A high volatile matter content means that high-proportion of fuel will be distilled and burned as a gas or vapour. The volatile matter present in the coal may be combustible gases (such as methane, hydrogen, carbon monoxide and other hydrocarbons) or non-combustible gases (like CO2 and N2). Volatile matter content is of special significance in coal gas manufacture and in carbonization plants, particularly when by-product recovery is the main object. Thus, high-volatile matter containing coals do not cake well; whereas medium-volatile matter content coals are capable of yielding hard and strong coke on carbonization.

- **(3) Ash** is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes. trouble during firing by forming clinker), which block the inters paces of the grate. This in-turn causes obstruction to air supply; thereby the burning of coal becomes *irregular.* Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. The presence of ash also causes early wear of furnace walls, burning of apparatus and *feeding* mechanism.

- **(4) Fixed carbon**: Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel.

Ultimate analysis

Carbon and hydrogen: About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

- $$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44}$$

- $$\text{Percentage of H} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample taken} \times 18}$$

Significance of ultimate analysis

- (1) **Carbon and hydrogen**: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible consti1fent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal.

- (2) **Nitrogen** has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.

Nitrogen: About 1 g of accurately weighed powdered 'coal is heated with concentrated H_2SO_4 along-with K_2S04(catalyst) in a long-necked flask(called *Kjeldahl's flask).* After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a *known volume of standard acid solution.* The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

- $$\text{Percentage of N} = \frac{\text{Volume of acid used x Normality x 1.4}}{\text{Weight of coal taken}}$$

Sulphur is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

- $$\text{Percentage of S} = \frac{\text{Weight of } BaSO_4 \text{ obtained x 32 x 100}}{\text{Weight of coal sample taken in bomb x 233}}$$

Ash determination is carried out as in proximate analysis.

Oxygen: It is obtained by difference.

- Percentage of O = 100 - Percentage of (C + H + S + N + ash)

- **(3) Sulphur**, although contributes to the heating value of coal, yet on combustion produces acids (S02 and S03), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% and derived from ores like iron pyrites, gypsum, etc., mines along-with the coal.
- Presence of sulphur is highly undesirable in coal to be, used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur (formed as combustion products) pollute the atmosphere and leads to corrosion.

- **(4) Oxygen** content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1. 7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen

METALLURGICAL COKE

Good coke for metallurgy should possess the following *requisites*

- (1) **Purity**: It should have moisture, ash, sulphur and phosphorus contents as low as possible. A low percentage of moisture helps in keeping down the heating expenses. Excess of ash hinders the heating and also helps in slag formation, which is not desirable in fuels. According to Dr. Mott, 2% of excess coke is required for the removal of 1 % ash. Presence of S and P gives on burning, undesirable products like SO2 P203 and P2O5, which adversely affect the quality of the metal being produced. Moreover, presence of sulphur makes the coke brittle.
- **(2) Porosity** : Coal should be porous, so that oxygen can easily come in contact with the carbon of coke, thereby helping in complete combustion at a high rate.
- **(3) Strength**: The coke should be quite compact, hard, strong to withstand dropping abrasion as well as the pressure of the over-burden (ore + fuel + flux) in the furnaces. It would be useless to employ weak coke in blast furnaces, as the weight of ore, etc., would crush the coke to breeze and thus prevent the essential passage of gases up the furnace.
- **(4) Size**: The size of metallurgical coke should be neither too big nor too small. In case the size is too big, the uniformity of heating is never maintained, but on the other hand, if the coke size is too small, choking will result.

- **(5) Cost**: Coke should be cheap and easily available near the site of the metallurgical plant, so that the transportation cost is low.

- **(6) Combustibility**: Coke should burn easily. The combustibility of coke depends upon the nature of the coal, carbonization temperature and reaction temperature. Cokes obtained from strongly coking coals are not as combustible as those derived from weakly caking and non-caking coals. At a given temperature, cokes obtained by high-temperature carbonization process are less combustible compared to those obtained by low-temperature carbonization. However, at high combustion temperatures (800° - 900°C), all cokes appears to be equally reactive. At about 1,000°C, it appears that the rate of combustion depends only on the rate of oxygen/air supply.
- **(7) Calorific value**: The calorific value of coke should be high.
- **(8) Low ash, S and P** contents to avoid the incorporation of these in the metal to be extracted.

- **(9) Reactivity to steam**: Reactivity towards steam increases with the reaction temperature and varies inversely with carbonizing temperature at which the coke was produces. Moreover, coke derived from non-caking coals are more reactive to steam than those derived from taking coals.

Coal versus coke in metallurgical processes

- (1) Coal does not possess as much strength and porosity as coke.
- (2) By coking, much of undesirable sulphur is removed.
- (3) Coke burns with short flame, due to expulsion of much of its
- volatile matter during carbonization.
- Because of these reasons, *"coke is preferred to coal for metallurgical purposes"*, particularly in blast furnaces. On the other hand, coal burns with a long flame, which is suitable only for reverberatory furnaces.
- Coking quality: The coals which on heating, in the absence of air, becomes soft, plastic and {use together to large coherent masses, are called **caking coals**. Consequently, such coals are difficult to be oxidized. If the residue (i.e.: coke) obtained after heating is porous, hard, strong and usable for metallurgical purpose, the original coal, is known as coking coal.

TYPES OF CARBONIZATION OF COAL

- These are *two* types of carbonization of coal:

- (1) **Low-temperature carbonization**: In this process, the heating of coal is carried our at 500 - 700°C. The yield of coke is about 75-80% and it contains about 5-15% volatile matter. *It is not mechanically strong, so it cannot be used as a metallurgical coke.* However, it burns easily giving practically a smokeless, hot and radiant fire. Hence, it is suitable for domestic purposes. The by-product gas produced (about 130-150 m3/tonne) by this process is richer in heating value (about 6,500-9,500 kcal/m3) and is, therefore, a more valuable gaseous fuel.

- (2) **High-temperature carbonization** is carried out at 900 - 1,200°C with the object of producing coke of the right porosity, hardness, purity, strength, etc., so that it can be used in metallurgy. Nearly all the volatile matter of coal is driven off and the yield of coke is about 65-75%, containing only 1-3% volatile matter. The by-product gas produced is high in volume (about 300-390 m3/tonne), but its calorific value is low (about 5,400-6,000 kcal/m3).

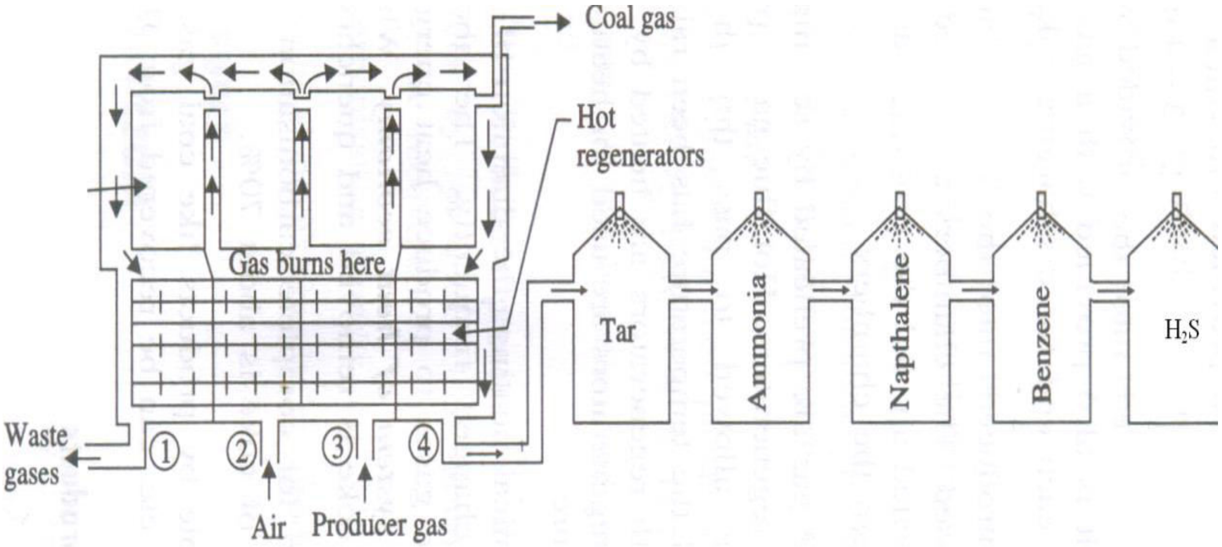
MANUFACTURE OF METALLURGICAL COKE

- **Otto Hoffman's by-product oven**:
- In order to: (1) *increase the thermal efficiency* of the carbonization process, and (ii) *recover valuable by-product* (like coal gas, ammonia, benzol oil, tar, etc.), Otto Hoffman developed modern by-product coke oven which, unlike beehive oven, is *heated externally* by a portion of coal gas produced during the process itself or by producer gas or by blast furnace gas. Moreover, the heating is done on the basis of *"regenerative system of heat economy", i.e.,* utilizing the waste flue gases for heating the checker-work of bricks.
- The by-product coke oven consists of number of narrow *silica chambers* (each about 10 to 12 m long, 3 to 4 m high and 0.40 to 0.45 m wide) erected side-by-side with *vertical flues* in-between them to form a sort of battery. Each chamber is provided with *a charging hole at the top, a gas off-take* and *a refractory-lined cast iron door* at each ends for discharging coke.

- A charge consisting *of finely crushed coal* is introduced through the charging holes at the top of chambers, which are then closed tightly at both ends to prevent any access of air. The coke ovens are heated to 1,200°C by burning gaseous fuel (like producer gas) and usually employing a regenerative principle to achieve as economical heating as possible. The flue gases produced during combustion, before escaping to chimney, pass on their *sensible heat* to one of the two sets of checker brick-work, until this brick-work has been raised to a temperature of about 1,000°C. The flow of heating gases is then *reversed* and the inlet gases are passed through the heated checker brick-work, which thus serves to preheat the inlet gases. The flue gases are then allowed to pass through the second set of checker bricks to heat it. This checker-work then serves to preheat the inlet gases. Thus, this cycle goes on. The heating is actually continued, till the evolution of volatile matter *ceases* completely. Carbonization of a charge of coal takes about between 11 to 18 hours.

- When carbonization is completed, a massive *ram* pushes the red hot coke into a truck. It is subsequently quenched by a water spray *('wet quenching').* In place of wet quenching, "dry quenching" offers advantages, because the coke produced is more strong, dense, graphitized and non-reactive. In this method, the red hot coke is placed in a chamber and cooled by passing inert gases from boilers (like nitrogen). The heated inert gases are then circulated to boilers, where they generate steam. The coke produced by 'dry quenching' is cheaper, drier and contains lesser dust than 'wet-quenched' coke.

Otto Hoffman's by-product oven



Recovery of by-products

(i)Recovery of tar : The gas is first passed through a tower in which liquor ammonia is sprayed. Here dust and tar get collected in a tank below, which is heated by steam coils to recover back ammonia sprayed. The ammonia is used again.

- **(ii) Recovery of ammonia**: The gases from the chamber are then passed through a tower in which water is sprayed. Here ammonia goes into solution as NH_4OH.
- **(iii) Recovery of naphthalene**: The gases are then passed through another tower in which water at very low temperature is sprayed. Here naphthalene gets condensed.
- **(iv) Recovery of benzene**: The gases are then sprayed with petroleum, when benzene and its homologues are removed.
- **(v) Recovery of H_2S** : The gases are then passed through a purifier, packed with moist Fe_2O_3. Here H_2S is retained.

$Fe_2O_3 + 3\ H_2S \qquad Fe_2O_3 + 3\ H_2O$

- After some time, when all Fe_2S_3 is changed into Fe_2O_3, the purifier is exposed to atmosphere, when Fe_2O_3 is regenerated,

$Fe_2S_3 + 4\ O_2 \qquad 2\ FeO + 3\ SO_2$

$4FeO + O_2 \qquad 2\ Fe_2O_3$

Liquid Fuels

The important liquid fuels are petroleum, petroleum products, tar, alcohols. These are naturally found under the sea surface. Liquid fuels are also obtained synthetically from' hydrogenation of coat. Liquid fuels find extensive use in domestic and industrial fields.

Petroleum

- Petroleum or crude oil is a dark greenish brown or black coloured viscous oil found deep in earth's crust. The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, 0 and S. The average composition of crude oil is C =80 - 87 %, H =11-15%, S = 0.1 -3.5%, (N +O) =0.1- 0.5%.

a) Classification of petroleum

- Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.
- i) Paraffinic-base type crude oil: It contains saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ and little amount of naphthalenes and aromatics.
- ii) Asphaltic-base type crude oil: It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.
- iii) Mixed-base type crude oil : It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.

Mining and Refining of Petroleum

- The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

- **Step -I: Separation of water (Cottrell's process)**
- The crude oil from the oil well is an extremely stable emulsion 0 f oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.

- **Step - II: Removal of harmful impurities**
- a) The presence of NaCI and MgCI in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.
- b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

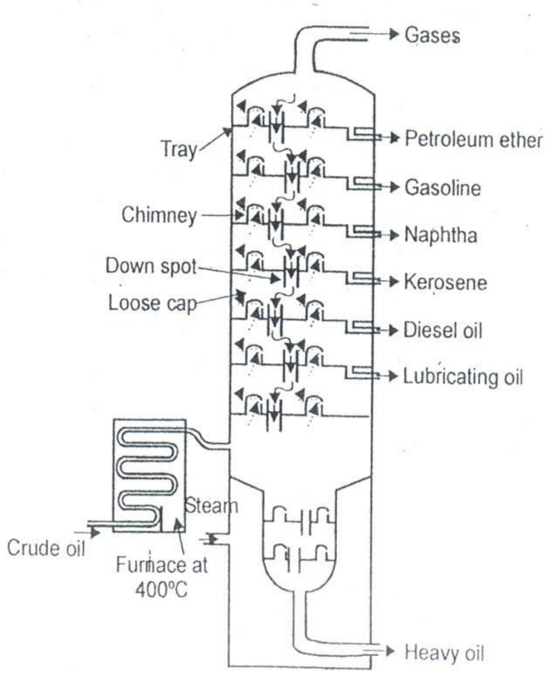
Fractional distillation

- **Step - III: Fractional distillation**

- The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. (Figure)

- When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.

Fractional distillation of Crude oil



Various fractions of crude oil and their composition and uses

S n .	Name of the fractions	Boiling range (^{O}C)	Composition of Hydrocarbons .	Uses
1.	Uncondensed gases	Below 30°C	C_1 to C_4	As domestic and industrial fuel under the name LPG
2.	Petroleum ether	30 70 °C	C_5 to C_7	As a solvent.
3.	Gasoline (or) petrol.	40 - 120 °C	C_5 to C_9	As motor fuel, solvent and in dry cleaning.
4.	Naphtha (or}solvent spirit .	120. - 180 °C	C_9 to C_{10}	As solvent and in dry cleaning.
5.	Kerosene oil.	180 - 250 °C	C_{10} to C_{16}	As fuel for jet engines and an illuminant.
6.	Diesel oil (or) gas oil	250 320 °C	C_{10} to C_{18}	As Diesel engine fuel.
7.	Heavy oil.	320 - 400 °C	C_{17} to C_{30}	Production of gasoline by cracking process.

Various fractions recovered from Heavy Oil

S n.	Name of the fractions	Boiling range (^{O}C)	Composition of Hydrocarbons.	Uses
1.	Lubricating oil	-	C_{17} to C_{20}	Used as lubricants
2.	Petroleum jelly (Vaseline)	-	-	Used in medicines and cosmetics
3.	Paraffin wax	-	C_{20} to C_{28}	Used in candles, wax paper, boot polish, etc
4.	Grease	-	-	Used as lubricants.
5.	Asphalt or bitumen	Above 400°C	C_{30} and above	Used for making roads, water proof roofing, etc

Cracking

- The decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight is called cracking.
- The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straight-run gasoline which is not good an_ hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process.
- The cracked gasoline gives better engine performance i.e., they are suitable for spark -ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons,
- There are two methods of cracking in use
- 1. Thermal cracking 2. Catalytic cracking

- **Thermal cracking** .
- In this process, the heavy oil is subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins and hydrogen. The cracked products are then separated by fractional distillation. This process is carried out in liquid phase at a temperature of 4 75 - 530° C and under pressure of 100 kg/cm2 is called Liquid-phase thermal cracking or at a temperature of 600-650°C (heavy oil is vapourised) and under a low pressure of 10-20 kg/cm2, such process is called Vapour-phase thermal cracking.

Catalytic cracking

- In this process, cracking is carried out in presence of a catalyst at lower temperature (300° C to 450° C) and pressures (l to 5 kg/cm2). The catalyst like aluminium silicate [$Al_2(SiO_3)$] or alumina [$A1_2O_3$] used in cracking gives higher yield and better quality of gasoline.
- There are two types of catalytic cracking in use .

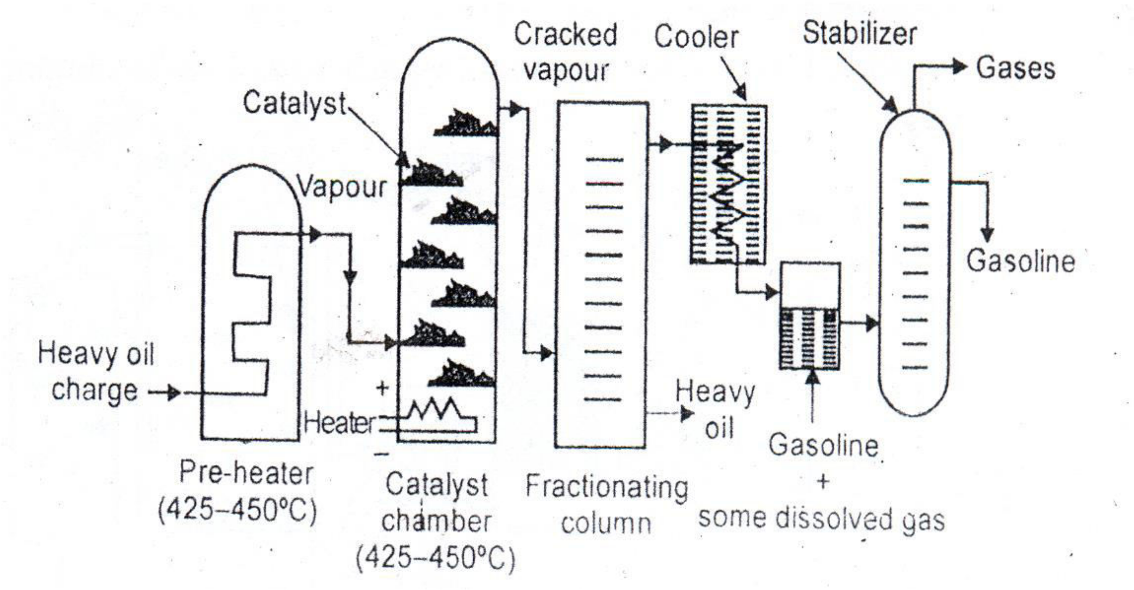
- **i) Fixed-bed catalytic cracking**
- The heavy oil is passed through the heater, where the oil is vapourised and heated to 400 to 500°C and then forced through a catalytic champers containing the catalyst of silica alumina gel (SiO_2, Al_2O_3) or bauxite, is mixed with clay and zirconium oxide maintained at 400 to 500°C and 1.5 kg/cm2 pressure. During their passage through the tower, cracking takes place about 30-40% of the charge is converted into gasoline and about 2-4% carbon is formed which gets deposited on the catalytic bed. (Figure)

- The vapours produced are then passed through a fractionating column, where heavy oil fractions condensed. The vapours are then admitted into a cooler, where some of the gaseous products are condensed along with gasoline 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 obtained.

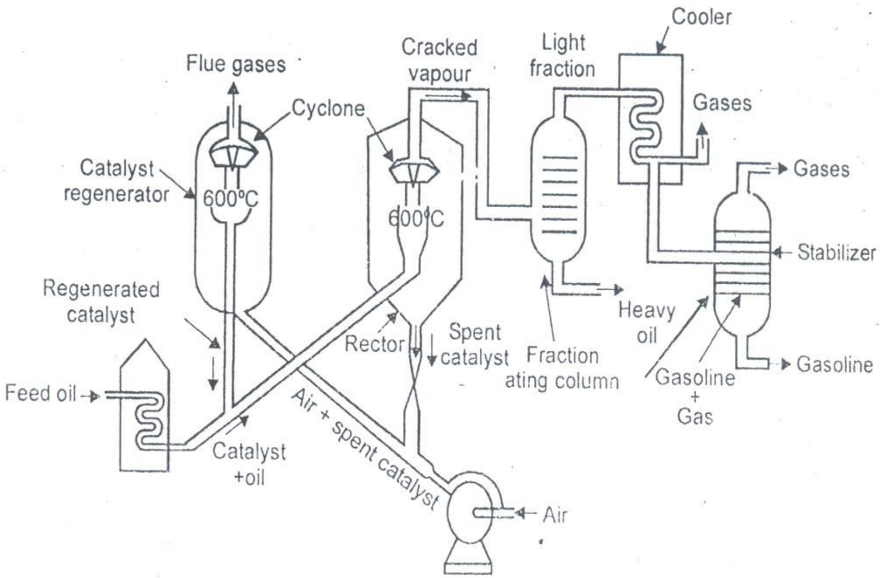
- When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber.

- **ii) Fluid (Moving)-bed catalytic cracking**
- In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530°C and pressure of about 3' to 5 kg/cm2. The top of the reactor, there is a centrifugal separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself. The carbon deposited on the catalyst powder are burnt off in the regenerator and the temperature rises to about 590°C or more. The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline. The product contains a higher proportion of aromatics and iso-paraffins.

Fixed-bed catalytic cracking



Fluid (Moving)-bed catalytic cracking



Knocking

- Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine.

- In a petrol engine, a mixture of gasoline vapour and air at 1: 17 ratio is used as fuel. This mixture is compressed and ignited by an electric spark. The products of oxidation reaction (combustion) increases the pressure and pushes the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem in knocking. But in some cases, the rate of combustion (oxidation) will not be uniform due to unwanted chemical constituents of gasoline. 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 reduces the efficiency of engine. So a good gasoline should resist knocking.

- **Chemical structure and knocking**
- The knocking tendency of fuel hydrocarbons mainly depends on their chemical structures. The knocking tendency decreases in the following order.
- Straight chain paraffins> Branched chain paraffins> Cycloparaffins > Olefins > Aromatics.

- **Improvement of antiknock characteristics**
- The octane number of fuel can be improved by
- (i) blending petrol of high octane number with petrol of low octane number, so that the octane number of the latter can be improved.

  (ii) the addition of anti-knock agents like Tetra-Ethyl Lead (TEL).

Anti-Knocking agent

- **LEADED PETROL (ANTI-KNOCK AGENT)**

- The anti-knock properties of a gasoline can be improved by the addition of suitable additives. Tetraethyl lead (TEL) or (C2H5)4 Pb is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

- TEL reduces the knocking tendency of hydrocarbon. Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

- **Disadvantages of using TEL**
- When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life. To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases.
- But this creates atmospheric pollution. So nowadays aromatic phosphates are used instead of TEL
- (iii) Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

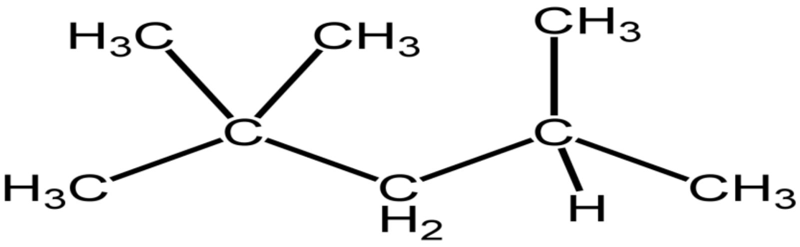
OCTANE NUMBER (or) OCTANE RATING

- Octane number is introduced to express the knocking characteristics of petrol. It has been found that n-heptane knocks very badly and hence, its anti-knock value has been given zero. On the other hand, iso-octane gives very little knocking and so, its anti-knock value has been given 100.
- ***Thus octane number is defined as 'the percentage of iso-octane present in a mixture of iso-octane and n-heptane.'***

n - heptane (Octane number = 0 anti knocking value)

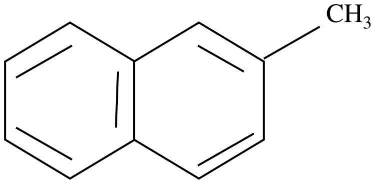
- CH3 – CH2 – CH2 – CH2 – CH2 – CH2 - CH3

Iso-octane (Octane number = 100 anti knocking value)



CETANE NUMBER (or) CETANE RATING

- Cetane number is introduced to express the knocking characteristics of diesel. Cetane has a very short ignition lag and hence its cetane number is taken as 100. On the other hand 2-methyl naphthalene has a long ignition lag and hence its cetane number is taken as zero.
- $CH_3 – (CH_2)_{14} – CH_3$
- n-cetane (hexa decane)
- cetane number = 100



- **2-methyl naphthalene (cetane number = 0)**
- Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl napthalene, which has the same ignition lag as the fuel under test".
- The cetane number decreases in the following order.
- n-alkanes > Cycloalkanes > alkenes >branched alkanes >aromatics
- The cetane number of a diesel oil can be increased by adding additives called dopes.
- **Important** dopes: *Ethyl nitrate, Iso-amyl nitrate.*
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Theoretical calculation of calorific value

- 1. Elements always combine in definite proportions to give. the products. For example 12 gm of carbon combines with 32 gm of oxygen to give 44 gm of CO2
- $C + O2 \xrightarrow{\hspace{3cm}} CO2$
- 12 32 44
- Similarly, 4gm of hydrogen combines with 32gm of oxygen to give 36gm of H2O.
- $2\ H2(g) + O(g) \xrightarrow{\hspace{3cm}} 2H2O(g)$
- 4 32 36

2. At STP (273 K, 1 atm) one mole of all gases occupy a volume of 22.4litres. Hence at S.T.P. 22.4 liters of CO2 will have a weight of 44gm, its molecular weight.

- 3. Air contains 21 % of oxygen by volume and 23 % of oxygen by weight, Hence 1 m3 of oxygen will be supplied by
- $$\frac{1 \times 100}{21} = 4.76\text{m3 of air}$$

- Similarly 1 kg of oxygen will be supplied by $\frac{1x100}{23}$ = 4.3 5 kg of air.
- 4. Molecular weight of air is 28.94mol-1.
- 5. Minimum oxygen required = (Theoretical O_2 required) - (O_2 present in fuels).
- 6. The mass of flue gas is calculated by balancing the carbon in the fuel and the carbon in the flue gas.
- 7. Minimum O_2 required is calculated on the basis of complete combustion of fuel. If as a result incomplete combustion or CO is formed then O_2 is calculated for the conversion of CO to CO_2.
- 8. If the fuel contains both O_2 and H_2, the amount of hydrogen and oxygen may be present in the form of as H_2O, which is a non-combustible substance. The remaining available hydrogen takes part in the combustion reaction.
- $2\ H_2(g) + O(g) \xrightarrow{\hspace{3cm}} 2H_20$

- 32 gm of oxygen combines with 4gm of hydrogen, Hence 1 part of hydrogen combines with 8 parts of oxygen.

- Hence, theoretical amount of oxygen required for complete combustion of 1 kg of fuel is given by the equation,
- {32/12 x C + 8[H – O/8] + S} kg

C, Hand S are masses of carbon. Hydrogen and sulphur respectively per kg of the fuel. Since 1 kg of air-contains 23%of oxygen by weight, the amount of air required theoretically to burn 1 kg of fuel completely is given by equation.

- 100/23 {32/12 x C + 8[H – O/8] + S} Kg

- According to Dulong's formula for the theoretical calculation of calorific value is,
- $$1/100\ [8080C + 34500\ (H - O/8) + 2240S]\ \text{Kcal/kg}$$
- Where C, H, O and S represent the % of the corresponding elements in the fuel. It is based on the assumption that the calorific value orc, Hand S are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely.
- However, all the oxygen in the fuel is assumed to be present in combination with hydrogen in the ratio H:O as 1:8 by weight. So the surplus hydrogen available for combustion is' $H - \frac{0}{8}$.
- NCV (or) LCV = [HCV – 9/100H x 587] kcal.kg

Theoretical calculation of minimum air requirement for combustion of a fuel

- Combustion is the process of burning any combustible substance in the presence of oxygen, which liberates energy in the form of heat and light. For efficient combustion, it is essential that the fuel must be brought into intimate contact with sufficient quantity of air or oxygen.
- The combustible substance usually present in fuels, which enter into the combustion, are mainly C, H, S and O. But N, CO2 and ash are incombustible matters present in the fuel, .do not take any oxygen during combustion.
- For the complete combustion of a given quantity of fuel can be calculated by considering the following point. Substances always combine in definite proportions, which are determined by the molecular weights of the substances.

- **i) Combustion of carbon**
- $C + O_2 \longrightarrow CO_2$

  12 32 44 (by weight)
- 12 parts by weight-of carbon requires 32 parts by weight of oxygen for complete combustion. 'C' parts by weight of carbon requires == 32 C /12 == 2.67 C
- (H- 0/8) parts by weight of hydrogen requires = $\frac{(H - O/8) \times 32}{4}$
- $= 8\,(H - O/8)$
- **ii) Combustion of hydrogen**
- . When oxygen is present in the fuel, it always combines with hydrogen. The combined hydrogen does not take part in combustion reaction. Therefore, the quantity of combined hydrogen must be deduced from the total hydrogen in the fuel.
- $2H_2 + O_2 \longrightarrow 2H_2O$
- 2 2 36 (by weight)

- 4 parts by weight of H_2 requires 32 parts by weight O_2 (or) 2 parts by volume of H_2 require 1 part by volume of O_2
- There fore 'H' parts by weight of hydrogen require $\frac{32x\ H}{4}$ parts by weight of O_2.
- iii) **Combustion of carbon monoxide**
- $CO + \frac{1}{2} O \longrightarrow CO_2$
- 28 16 (by weight)
- 1 0.5 (by volume)
- 1 volume of CO requires 0.5 volume of oxygen.

- **iv) Combustion of sulphur**
- S + $O_2 \xrightarrow{\quad} SO_2$
- 32 32 (by weight)
- 1 1 (by volume)
- 1 volume of 'S' requires 1 volume of oxygen.
- **v) Combustion of methane**
- $CH_4 + 2O_2 \xrightarrow{\quad} CO_2 + 2 H_20$
- 16 64 (by weight)
- 1 2 (by volume)