UNIT- III

FOSSIL FUELS -1

Energy is a essential part of life. Better energy sources are status symbol of a country. Fuels are mainly the energy sources for the industry and domestic purposes. For many years to come, the greatest portion of the world's power will come from the combustion of fuels.

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes.

Ex: Wood, Charcoal, Coal, Kerosene, petrol, Diesel, Producer gas, Oil gas etc... are some of the fuels.

The combustion is a quick, high temperature oxidation of fuels, converting carbon to CO_2 and hydrogen to water with the evolution of heat and light. During the process of combustion of a fuel (like coal) the atoms of carbon, hydrogen etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the "rearrangement of valancy electrons", in these atoms, resulting in the formation of new compounds (like CO_2, H_2O etc.), these new compounds have less energy (or heat content) in them and, therefore, the energy (or heat) released during the combustion process is the difference in the energy of the reactants (C, H and O etc., of fuel) and that of the products formed.

$$\text{Fuel} \longrightarrow \text{heat energy} + \text{light} + \text{combustion products}$$

The main source of fuels is coal and petroleum oils, the amounts of which are dwindling day -by -day. These are stored fuels available in earht's crust and are, generally called "fossil fuels. Now a days different type of fuels are available.

FUEL

- Bio fuels [Biomass (solid) Bio gas (liquid)]
- fossil fuels [petroleum products]
- nuclear fuels [$_{92}U^{235}$, $_{94}Pu^{239}$] U=uranium Pu= plutonium

Classification of fuels:-

Classification of fuels is based on two factors.

1. The way it is obtained (natural or artificial)
2. Physical state of the fuel (solid, liquid, gas).

Based on above said factors, fuels are classified into 2 types

1) **Natural fuels (primary fuel):-**
   Some fuels are found in nature and are used in the same form are called natural fuels, or primary fuels.
   Ex:-wood, coal and natural gas, petroleum oil (crude oil).
2) **Artificial fuel (secondary fuel):-**
   Some of the fuels that are derived from other fuels (primary) are called artificial or secondry fuels.
   Ex: - petrol and charcoal.

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Fuel

Natural (primary) fuel
- Solid (coal)
- Liquid (crude oil) (or) Petroleum oil
- Gas (Natural) Gas

artificial (secondary) fuel
- Solid (Charcoal) coke
- Liquid (Petrol, diesel, kerosene)
- Gas (coal gas, CNG, LPG, Biogas)

Comparison of solid, liquid and gaseous fuels:-

Solid	Liquid	Gas
Cheap and easily available	Costly and available only in the Arabic countries and obtained from wells	More costly except natural gas
As it does not burn spontaneously , its storage and transportation is easy	Transportation easy and storage needs care	Transportation is easy but storage is risky
Fire hazards are least	More risky	More risky
Slow combustion	Quick combustion	Very fast combustion
Ash content is more	No ash content	No ash content
Causes more pollution	Less pollution	Least pollution
Low calorific value	Higher calorific value	Highest calorific value
More oxygen is required for combustion	Less O_2 is required for combustion	Least O_2 is required for combustion
It cannot be used in vehicles as fuel	Mainly used in vehicles as fuel	Also used as fuel for vehicles

CALORIFIC VALUE:-

The calorific value of any fuel is a very important property. It measures the heat produced by the fuel. Higher the calorific value better will be the fuel.

It is defined as **"the amount of heat produced by the combustion of unit mass or unit volume of a fuel".**

The calorific value is measured in several units of heat; they are calorie, kilocalorie, British thermal unit (B.T.U) and centigrade thermal units (CTU) or Centigrade Heat Unit (CHU). Relationship among all the above units of heat is given below.

1 kcal = 1000 cal = 3.968 BTU = 2.2 CHU (or) CTU

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Joule is also a unit of heat or energy.

1 Cal = 4.18 Joule.

There are two types of calorific values of a fuel

1. High Calorific Value (HCV) or Gross Calorific Value (GCV)
2. Low Calorific Value (LCV) or Net Calorific Value (NCV)

High Calorific Value (HCV) or Gross Calorific Value (GCV):-

It is defined as "the total amount of heat produced, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature."

Usually, all fuels contain some hydrogen and when the calorific value of hydrogen – containing fuel is determined experimentally the hydrogen is converted into stream. 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 HCV or GCV.

2 .Low calorific value (or) Net calorific value:-[LVC (or) NCV]

It is defined as "the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the products are permitted to escape".

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

Relationship between HCV and LCV:-

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$$

If hydrogen is present in a fuel, the above –mentioned chemical reaction will take place and 2g of hydrogen will produce 18g of H_2O (or) 1g of hydrogen will produce 9g of H_2O. if x g hydrogen is present in a fuel, it will produce 9x gr of water [because 1 part by mass of hydrogen produces 9 parts by mass of water]; and 9x gr of water vapour that will release 9x X 587 cal/g heat on cooling,[L cal/g is the latent heat of water vapour].

So,

$$LCV = HCV - \text{latent heat of water vapour formed (or)}$$

$$LCV = HCV - 9XL$$

Further,

$$HCV = LCV + 9XL$$

In case hydrogen is H%, the above relation will be;

$$HCV = LCV + 0.09\, H \times 587$$

$$LCV = HCV - 0.09H \times 587\ \text{Kcal/Kg}$$

x= mass of hydrogen L= latent heat of water vapour, the latent heat of steam os 587 Kcal/Kg (or) 1,060 BTU/lb of water vapour at room temperature.

It is generally expressed in calorie/gram (cal/g) or kilol calorie/kilogram (Kcal/kg) or British thermal unit/lb (BTU/lb) in case of solid or liquid fuel. In case of gaseous fuels, the units used are kilo calorie/cubic meter (Kcal/m^3) or BTU/cubic feet (BTU/ft^3).

Characteristics of a good fuel:-

A good fuel has the following features:

1. It should be easily available
2. It should be dry and should have less moisture content. Dry fuels increase its calorific value.
3. It should be cheap, poor people cannot afford costlier fuel.
4. It should be easily transportable; otherwise cost of fuel will increase.
5. It must have high calorific value.
6. It must have less ash after combustion. Incase of more ash, the fuel gives less heat.

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4. It should be easily transportable; otherwise cost of fuel will increase.
5. It must have high calorific value.
6. It must have less ash after combustion. Incase of more ash, the fuel gives less heat.

7. It must have moderate ignition temperature. Low burning (or) ignition temperature can cause fire accident.
8. It should not burn spontaneously to avoid fire hazards.
9. It should not give poisonous gases after combustion
10. Its handling should be easy.
11. The combustion of a good fuel should not be explosive.

Determination of calorific value:- Not in syllabus.

Calorific value of solid and liquid fuels are determined by "Bomb-Calorimeter". The calorific value of gaseous fuels determined by Junker's Method.

Determination of calorific value by Bomb Calorimeter:-

The bomb calorimeter is a device that is used for the determination of calorific values of the solid and liquid fuels. Since combustion of fuel is explosive, it is called the bomb calorimeter.

A bomb calorimeter is made of a cylindrical stainless steel vessel called bomb. It contains a crucible having known mass or volume of a fuel fixed on a screw. A magnesium fuse wire is connected to the electrodes and the electrodes are connected to a 6V battery. A copper calorimeter envelops the bomb. The calorimeter has known amount of water having stirrer and Beckman's thermometers. There are two jackets around the calorimeter, i.e. air and water, as shown in figure to prevent heat radiation.

As battery is connected to the electrodes, current flows through Mg wire, which ignites the fuel (cotton or cotton thread is also sometimes used for ignition of fuel). The initial and final temperatures of water in the calorimeter are measured with the Beckman's thermometer.

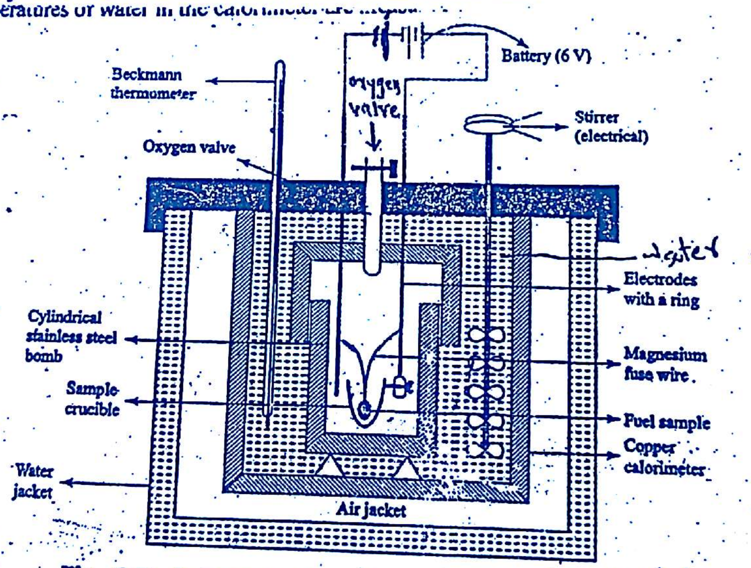

Fig. 6.3 Schematic diagram of a bomb calorimeter

Calculation of the calorific value:-

Mass of fuel	= m g
Mass of water in calorimeter	= W g
Water equivalent of calorimeter	= w g
Initial temperature of water	= T_1° C
Final temperature of water	= T_2° C

the corresponding acids (H_2SO_4, HNO_3). They will give some additional heat (C_A) and that must be subtracted from the heat. The reaction is exothermic.

$$S + H_2 + 2O_2 \longrightarrow H_2SO_4 + Heat$$

$$N_2 + H_2 + 3O_2 \longrightarrow 2HNO_3 + Heat$$

4. **Cooling correction (T_c):** The process of cooling will not give the correct temperature difference. The temperature difference (T_2-T_1) must be higher than what is observed. So cooling correction should be added to the temperature raised. The cooling correction, T_c, is numerically equal to the total time required in cooling from T2 to T1(time T multiplied by ΔT i.e. rate of cooling per minute).

$$T_c = \Delta T \times T \qquad (T=Time)$$

Considering all the above corrections, the formula for calorific value will be modified as given below.

$$HCV = \frac{(w+W)(T_2-T_1+T_c)-(C_f+C_c+C_A)}{m} \text{ cal/g}$$

Theoretical Calculation of Calorific Value by Dulong's formula: Syllabus

The calorific value of fuel can be approximately computed by noting the amount of the constituents of the fuel. The higher calorific value of some of the chief combustible constituents of fuel are tabulated below.

Constituent	Hydrogen	Carbon	Sulphur
HCV(kcal/kg)	34,500	8080	2240

The oxygen if present in fuel it is assumed to be present in combined form with hydrogen, i.e. in the form of water. So, the amount of hydrogen available for combustion

= Total mass of hydrogen in fuel – Fixed hydrogen

= Total mass of hydrogen in fuel – (1/8) Mass of oxygen in the fuel

(Since, 8 parts of oxygen combine with one part of hydrogen to form H_2O).

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

$$HCV = \frac{1}{100}\left[8080\,\%C + 34500\left(\%H - \frac{\%O}{8}\right) + 2240\,\%S\right] \text{Kcal/Kg}$$

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

$$LCV = \left[HCV - \frac{9}{100} \times \%H \times 587\right] \text{Kcal/Kg (or) } \left[HCV - 0.09\,H\% \times 587\right] \text{Kca}$$

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.

SOLID FUELS: - (COAL)

WOOD: - Wood is obtained from forests. Freshly cut wood contains 25 to 50% moisture, which is reduced to about .15% on air-drying. The average composition of wood on dry moisture-free-basis is: carbon = 50%, Hydrogen = 6%; Oxygen = 43%, ash = 1%. The calorific value of air-dried-wood is about 3,500 to 4,500 Kcal/Kg.

COAL: -

Because of the environmental hazards, the trees were buried inside the earth. By the temperature, pressure and bacterial actions, they were converted into a brown-black solid named coal, in thousands of years.

$$\text{Wood} \xrightarrow[\text{Bacterial actions}]{\text{Temperature / Pressure}} \text{Coal}$$

The process of conversion of wood into coal is called "Coalification". Depending upon the percentage of carbon, hydrogen, moisture and calorific value, four different types of coals exist. It is called "Ranking of coal"

Wood → Peat → Lignite → Bituminous coal → Anthracite.
(Coal)

This progressive transformation of wood to anthracite results in,

a) Decrease in the moisture content.
b) Decrease in hydrogen, oxygen, nitrogen and sulphur contents, with a corresponding rise in carbon content.
c) Decrease in volatile matter content.
d) Increase in the calorific value.
e) Increase in hardness.

1) **Peat: -** Peat is brown fibrous jelly-like mass. It is regarded as the first stage in the coalification of wood. Peat is mostly dug by manual labour. It is uneconomical fuel, since it may contain as much as 80-90% water, but on air-drying (after 1 to 2 months drying), it burns freely. The average composition of air-dried peat is c = 57%, H= 6%, o = 35%, ash content is 2.5 - 6%. Its calorific value is about 5,400 Kcal / Kg.

2) **Lignites : - (Brown Coals)** These are soft, brown coloured variety of lowest rank coals, which consist of vegetable matter decomposed more than that in peat. It

consists of 20-60% of moisture and on air-drying; it breaks up into small pieces. Air-dried Lignite contains, C = 60-70%, H= 5%, O = 20%. The calorific value is about 6,500 – 7,100 Kcal/Kg.

3) **Bituminous Coals : - (Common Coals):**

These are pitch-black to dark-gray coals, which usually soil hands. They show a laminated structure of alternate very bright and dull layers. The common bituminous coals are sub-classified on the basis of carbon content.

a) **Sub-bituminous Coals: -** These are black in color and more homogeneous and smooth in appearance. Carbon content varies from 75% to 83 % and oxygen from 10% to 20%. The calorific value is about 7000 – 7500 K cal / Kg.

b) **Bituminous coals:-** These can show a typically banded appearance and carbon content ranges from 78%-90% their calorific value is 8,000-8,500 Kcal/Kg.coal of this class is used in the large quantities in industries for making metallurgical coke, coal gas and for steam raising and domestic heating.

c) **Semi- bituminous coals:-** These included varieties of bituminous coals that are rich in carbon (90-95%) and have low volatile matter. their calorific value is about 8500-8600Kcal/Kg.

4) **Anthracite :-** it is a class of highest rank coal, containing higest percentage of carbon (92-98%) and has lowest volatile matter and moisture content they are hardest of all kinds of coals, quite dense and lustrous in appearance their calorific value is about 8,650-8,700 Kcal/Kg and ash content is very small (about 3%),

Change in the average composition from wood to anthracite,

Fuel	Moisture of air-dried sample at 40° C (%)	C	H	N	O	CALORIFIC VALUE Kcal/Kg
Wood	25%	50	6	0.5	43.5	3500 - 4500
Peat	25%	57	5.7	2	35.3	4125 - 5400
Lignite	20%	67	5	1.5	26.5	6500 - 7100
S.B.coal	11%	77	5	1.8	16.2	7000 - 7500
B.coal	4%	83	5	2	10	8000 - 8500
Semi.B.C	1%	90	4.5	1.5	4	8500 - 8600
Anthracite	1.5%	93.3	3.0	0.7	3.0	8650 - 8700

Analysis of Coal:-

The analysis of coal is helpful in its ranking. The assessment of the quality of coal is carried out by these two types of analyses.

1. **Proximate Analysis**
2. **Ultimate Analysis**

1. **Proximate Analysis: -** In this analysis, the percentage of carbon is indirectly determined. This analysis includes percentage of moisture, % of volatile matter, % of ash content and % of carbon.

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a) **Moisture: -** A known mass of finely powdered coal is taken in a crucible. It is heated up to 110^0 C in an electric hot air-oven. The crucible 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.

$$\% \text{ of Moisture} = \frac{\text{Loss in Weight of Coal} \times 100}{\text{Weight of Coal taken}}$$

b) **Volatile matter: -** The above sample is taken and heated at 950^{0}c in an electric furnace in the absence of air for 7 minutes. It is then cooled to room temperature and weighed. The loss of weight is reported as volatile matter and is removed from coal at 950^{0}c.

$$\% \text{ of Volatile Matter} = \frac{\text{Loss in weight of coal due to removal of volatile matter} \times 100}{\text{Weight of Coal taken}}$$

c) **Ash Content: -** In this analysis, the above coal, free from moisture and volatile matter, is heated in a crucible at about 700^{0}c in the presence of air. It undergoes combustion and results in the formation of ash. Crucible is cooled to room temperature and weighed. The weight of ash is then determined.

$$\% \text{ of Ash} = \frac{\text{Weight of Ash left} \times 100}{\text{Weight of Coal taken}}$$

d) **Carbon :-** Since main component of coal is carbon, it can be determined by subtracting the sum of percentage of moisture , volatile substance and ash content from 100.

% of Carbon = 100 – (% of moisture + % of volatile matter + % of ash)

Importance or Significance of Proximate Analysis:-

Proximate analysis provides following valuable informations in assessing the quality of coal.

Moisture: - High moisture content in the fuel reduces the calorific value,increases the cost of transportation and causes wastage of heat. Hence, the lesser the moisture content, the better is the quality of a fuel.

Volatile matter: - A coal containing high volatile matter burns with long flame, high smoke and low calorific value. Volatile matter also influences the design of furnace since the higher the volatile matter, larger is the combustion space required.

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Ash:- It is a useless, non- comustible matter, which reduces the calorific value of coal, ash content also increases cost of transportation, handling and storage and disposal. It determines the quality of coal .Hence the lesser the percentage of ash, the better is the quality of coal.

Carbon:- The higher the fixed carbon in a coal, the greater is its calorific value.

2. ULTIMATE ANALYSIS:-

This analysis includes percentage of C,H,O,S,N and ash content in coal.

(a) Carbon and hydrogen determination :-

A known weight (1-2gr) of coal is taken and burnt in an apparatus. The carbon change to CO_2 and hydrogen changes to H_2O. The vapours of CO_2 and H_2O are then passed through KOH and $CaCl_2$. The CO_2 is absorbed by KOH in the tube while H_2O is absorbed by $CaCl_2$. Because of the absorption, the weight of KOH and $CaCl_2$ increases, which is measured.

$$\underset{(12)}{C} + O_2 \xrightarrow{\text{Ignition}} \underset{(44)}{CO_2}$$

$$\underset{(2)}{H_2} + \tfrac{1}{2}O_2 \xrightarrow{4} \underset{(18)}{H_2O}$$

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

$$CaCl_2 + H_2O \longrightarrow CaCl_2 \cdot H_2O$$

$$\text{Percentage of carbon} = \frac{\text{increase in weight of KOH}}{\text{weight of coal (1-2 gr)}} \times \frac{12}{44} \times 100$$

$$\text{Percentage of Hydrogen} = \frac{\text{increase in weight of cacl2}}{\text{weight of coal (1-2 gr)}} \times \frac{2}{18} \times 100$$

Significance: - The higher the percentage of carbon and hydrogen, the better is the quality of coal and higher its calorific value. Percentage of carbon helps in assessing the rank of coal.

(b) Nitrogen determination: - The estimation of nitrogen is done by kjeldahl method

(i) About 1 gr of accurately weight powdered coal is heated with conc. H_2SO_4 along with K_2SO_4

(ii) When clear solution is obtained (i.e, when whole nitrogen is converted into ammonium sulphate) it is treated with excess of NaOH to liberate ammonia.

(iii) The ammonia thus produced is distilled over and absorbed in a known volume of standard H_2SO_4 solution.

(IV) The volume of unused H_2SO_4 acid is then determined by back titration with standard NaoH solution [un used H_2SO_4 means unreacted H_2SO_4]

$$\text{Percentage of Nitrogen} = \frac{\text{Volume of } H_2SO_4 \text{ Consumed} \times \text{Normality} \times 1.4}{\text{Weight of Coal taken (1gr)}}$$

Significance: - Nitrogen does not have nay calorific value. It has no significance, thus, a good quality coal should have very little nitrogen content.

(C) Sulphur determination: - A known amount of coal is burnt completely in bomb calorimeter in a current of oxygen, by which sulphur present in coal is oxidized to sulphates. The ash from the bomb calorimeter is extracted with dil.HCl. The acid extract is then treated with $BaCl_2$ solution to precipitate sulphate as $BaSO_4$. The ppt of $BaSO_4$ is filtered, washed, dried and heated to constant weight.

$$\text{Percentage of sulphur} = \frac{\text{weight } BaSO_4 \times 32 \times 100}{\text{weight of coal} \times 233}$$

Atomic weight of S=32; molecular wt of $BaSO_4$ = 233

Significance: -

(a) Sulpher increases calorific value.

(b) The product of combustion SO_2, SO_3 have corrosive effect on equipment, and cause air pollution.

(c) Sulphur is undesirable in the preparation of metallurgical coke for iron industry, since it is transferred to the iron metal and body affects the quality and properties of steel.

(d) Ash determination: - Ash determination is carried out as in proximate analysis. The coal sample free from moisture and volatile matter is heated in a crucible at about 700^{0}c in the presence of air. It undergoes combustion and result in the formation of ash. Crucible is cooled to room temperature and weighed. The weight of ash is then determined.

$$\text{Percentage of ash} = \frac{\text{weight of ash left}}{\text{weight of coal taken}} \text{X}100$$

Significance: - It is a useless, non- combustible matter, which reduce the calorific value of coal. Ash content also increases cost of transportation, handling and storage and disposal. It determines the quality of coal. Hence, the lesser the percentage of ash, the better is the quality of coal.

(e) Oxygen determination: - The % of oxygen is determined by subtracting the sum of percentage of C,H,S,N and ash from 100.

Percentage of oxygen = 100 – [percentages of C+H+N+S+ash]

Significance: - Oxygen content decreases the calorific value of coal. High oxygen – content coals are characterized by high inherent moisture, low calorific value. An increase in 1% oxygen content decrease the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

Numericals related to Combustion (By weight & By volume air required), Bomb Calorimeter, Dulongs formula.

COMBUSTION :-

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Combustion is an exothermic chemical reaction, which is accompanied by development of heat and light at a rapid rate, so that temperature rises continuously and considerably.

For example, Combustion of Carbon in oxygen;

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

Ignition temperature :-

For proper combustion, the substance must be brought to its 'Kindling' or Ignition temperature, which may be defined as " the minimum temperature at which the substance ignites and burns without further addition of heat from outside".

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FUELS - 2

Liquid fuels :- (Petroleum)

Petroleum is one of the best primary liquid fuels. It is also known as crude oil. Petrol, diesel, kerosene are main liquid fuels. They are secondary liquid fuels derived from petroleum. These fuels are used for domestic works, auto vehicles and power generation.

The word meaning of petroleum is 'rock oil' (Petra = rock; oleum = oil; petroleum is dark brown viscous liquid. Petroleum is a mineral found deep in earth's crust, it is a mixture of number of hydrocarbons (paraffins olefins, aromatics, and naphthalene), nitrogen, sulphur, and oxygen containing optically active compounds along with traces of compounds of heavy metals like Fe, Co, Ni, and V.

Composition of petroleum is given as:

C= 80 - 87.1% H= 11.1 – 15.0% S=0.1 – 3.5% O=0.1 – 0.9% N= 0.4 – 0.9%

Refining of crude oil: **- [*Fractional Distillation of Crude Oil*]**

The crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The process is called refining of crude oil, and the plants set up for the purpose, are called the oil refineries. The process of refining involves the following steps.

Step 1:- [separation of water]

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water is separated from oil in the form of big droplets.

Step 2:- [Removal of harmful sulphur compounds]

The crude oil is treated with copper oxide (CuO) which gives black precipitate of copper sulphide which can be removed by filtration.

Step 3:- [fractional distillation]

Crude oil obtained after step 1 and step 2, is then heated at about 400^0 c in an iron resort, where by all volatile constituents except the residue (asphalt or petroleum coke) are evaporated. The hot vapours are then passed up a "fractionating column" which a tall cylindrical tower is containing a number of horizontal stainless steel trays, at short distances each tray is provided with small chimney, covered with a loose cap. As the vapour go up. They become gradually cooler and fractional condensation takes place at different heights of column, higher boiling fraction condenses first, while the lower boiling fractions turn – by-turn.

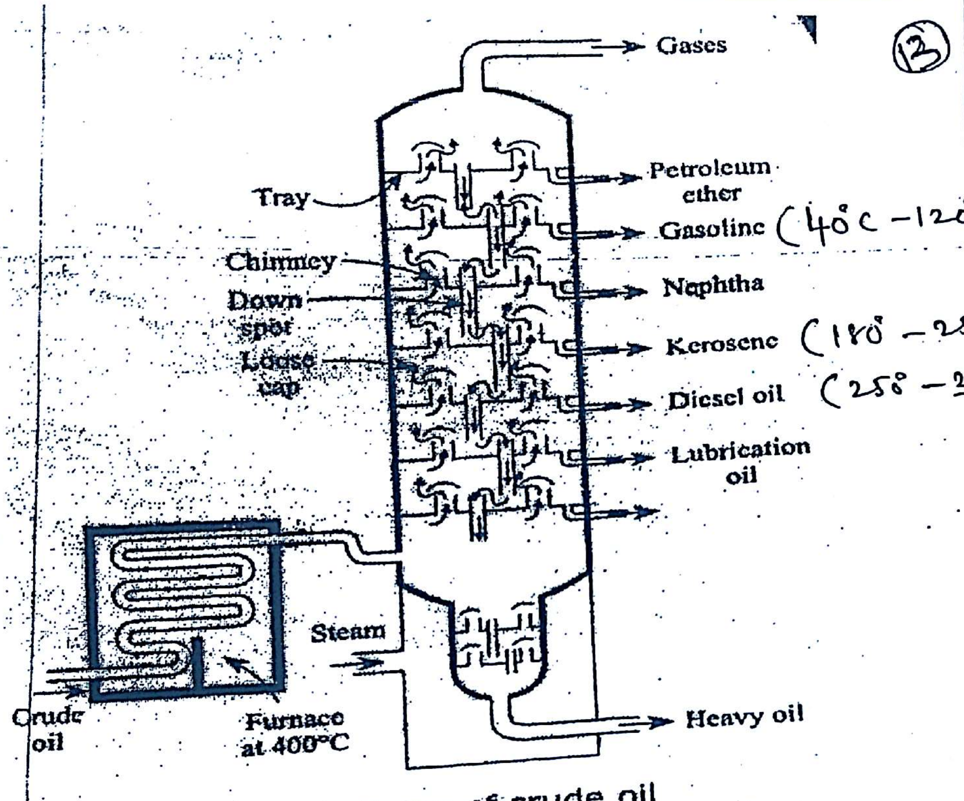


Fig. 6.7 Refining of crude oil

A brief description of three most important liquid fuels derived from petroleum is given on below:

A. **Gasoline or petrol:** It is obtained between $40^0 - 120^oc$ and is a mixture of hydrocarbons such as C_5H_{12} (pentane) to C_8H_{18} (octane). Its approximate composition is: C=84%, H=15%, N+S+O = 1%. Its calorific value is about 11,250 kcal/kg. It is highly volatile, inflammable and used as fuel for internal combustion engines of automobiles and aeroplanes.

B. **Kerosene oil:** It is a fraction obtained between $180^0 - 250^oc$ and is a mixture of $C_{10}H_{22}$ (decane) to $C_{16}H_{34}$ (hexadecane) hydrocarbons. Its approximate composition is: C=84%, H=16%, with less than 0.1% Sulphur. Its specific gravity is 0.75 - 0.85. Its calorific value is 11,100 kcal/kg. Due to high boiling point range, kerosene does not vaporise easily. It is used as domestic fuel in stoves, as jet engine fuel and for making oil gas.

C. **Diesel oil:** It is a fraction obtained between $250^0 - 320^oc$ and is a mixture of $C_{15}H_{32}$ (pentadecane) to $C_{18}H_{38}$ (octadecane) hydrocarbons. Its density is 0.86 – 0.95. Its calorific value is about 11,000 kcal/kg. It is used as a diesel engine fuel.

Cracking:-

Cracking is a process of conversion of bigger hydrocarbon molecules into smaller hydrocarbons of lower molecular weights.

Eg: - $C_{10}H_{22}$ $\xrightarrow{\text{cracking}}$ C_5H_{12} + C_5H_{10}

(decane) (n-pentane) (pentene)

B.P = 174^0 C Saturated Hydrocarbon unsaturated Hydrocarbon

B.P=36^0 C

Of all the fractions obtained by fractionation of petroleum oil, gasoline has the largest demand as a motor fuel, but the yield of this fractions is only 20% of the crude oil. Also the quality of so – called "straight – run" gasoline is not high. It has to be properly blended. Moreover, there is a surplus of heavier petroleum fractions.

To overcome these difficulties, the middle oil and heavy oil are cracked to get petrol. The petrol made by cracking has far better characteristics than "straight-run" petrol.

The process oil cracking is mainly of two types.

(1) Thermal cracking

(2) Catalytic cracking

Catalytic cracking: The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminum silicate [$Al_2(sio_3)_3$], aluminum oxide [Al_2O_3] or [ZrO_2 + artificial clay]. This process completes at lower temperatures and lower pressure when compared to the thermal process. Catalytic cracking is of two types.

[300°c – 450°c & 1.5 Kg/cm²].

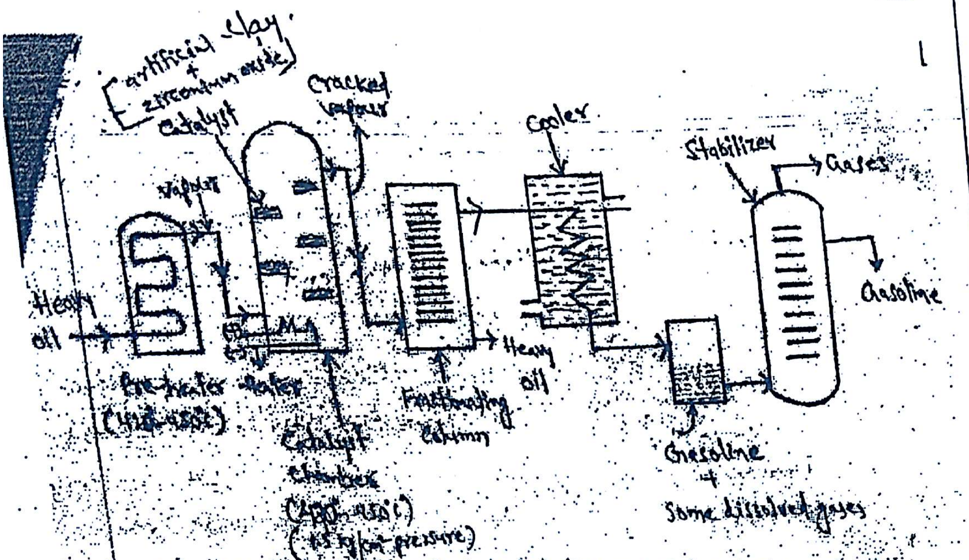
(a) Fixed-bed catalytic cracking

(b) Moving-bed catalytic cracking

(a) Fixed – bed catalytic cracking:-

The oil vapour are heated in a preheater to cracking temperatures (420^0-450^0c) and then forced through a catalytic chamber (containing artificial clay mixed with zirconium oxide) maintained at 425^0 – 450^0c and 1.5 Kg/cm^{2}pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2-4% carbon is formed. The latter gets adsorbed on the catalyst bed. The vapours produced are then passed through a fractionating column, where heavy oil fractions condense. The vapours are then led through a cooler, where some of the gases 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.

catalyst, after 8-10 hours, stops functioning, due to the deposition of black layer of bon, formed during cracking. This is re-activated by burning of the deposited carbon. ring the re- activation, the vapours are directed through another catalyst chamber. (15)



* Fixed – bed Catalytic Cracking *

KNOCKING

In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel. After the initiation of the combustion reaction by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture, there by the expanding gas drives the piston down the cylinder.

The efficiency of an engine is directly related with compression ratio (CR)," The ratio of the gaseous volume in the cylinder at the end of the suction – stroke to the volume at the end of the compression – stroke of the piston, is known as "compression ratio; more CR value better will be engine". CR depends upon the type of constituents in gasoline.

"In certain circumstances (due to the presence of some constituents in the gasoline used), the ratio of oxidation becomes so great that the last portion of the fuel – air mixture gets ignited instantaneously (immediately), producing an explosive violence, known as knocking". Knocking decreases the efficiency of engine.

The tendency of knocking is based on the chemical structure of hydrocarbons.

Straight- chain paraffins > branched – chain paraffins > olefins > cyclo paraffins > aromatics

In the above order, the knocking of fuel constituents decreases and anti – knocking increases from left to right.

The anti- –knocking value of fuel can be increases by adding tetra ethyl lead (TEL)--- [$(C_2H_5)_4Pb$]. and MTBE. [Methyl tertiary butyl ether]

Fuel rating:-

Octane number (or) octane Rating:- Knocking of fuel (gasoline), can be measured in terms of octane number (or) octane rating, it has been found that n-heptane knocks very badly hence , its anti – knock value has arbitrarily been given "zero". On the other hand, isooctane (2,2,4-trimethyl pentane) gives very little knocking so its anti – knocking value has been given as "100".

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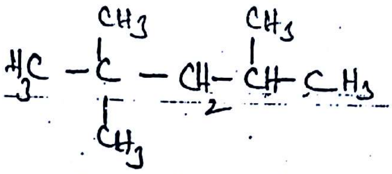
$H_3C-(CH_2)_5-CH_3$

(octane No is '0')
n-heptane



Isooctane (octane No = 100).

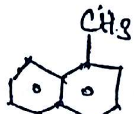
"octane number of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of isooctane- and n- heptane, which matches the fuel under test in knocking characteristics". In this way, an '80- octane" fuel is one which has the same combustion characteristics as a 80:20 mixtures of isooctane & n- heptanes.

Cetane number or rating: The knocking characteristics of diesel oils are usually expressed in terms of cetane number($C_{16}H_{34}$) are also called as n-hexadecane. It is a saturated hydrocarbon having a short ignition lag as compared to any commercial diesel fuel. Its cetane number is 100. It ignites below compression temperature.

α–methyl naphthalene has a very long ignition lag as compared to any commercial diesel oil. Its cetane number is taken as zero.

$H_3C-(CH_2)_{14}-CH_3$

n-hexadecane (Cetane)
Cetane No = 100



α-methyl naphthalene
Centane No = 0

In diesel engine, fuel is exploded not by spark but by temperature and pressure. The suitability of diesel fuel is determined by its cetane number.

Cetane number is the percentage of n-hexadecane in n-hexadecane and α–methyl naphthalene which has the same ignition characteristics as that of the sample under test. Cetane number 60 means, it has the same ignition characteristics as that of 60 parts of cetane and 40 parts of α–methyl naphthalene. The order of cetane number for the following is given as

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

→ Increasing order of Anti Knocking

Unleaded Petrol:

Octane rating of petrol is in leaded petrol is increased by adding tetra ethyl lead or tetra methyl lead. However, combustion of lead petrol leads to formation of litharge (PbO), which deposition the inner wall of cylinder and jams the piston. Also leaded petrol cannot be used in automobiles equipped cost catalytic converter, because lead present in exhaust gas poisons the catalyst, thereby destroying the active sites.

Alternative method of increasing octane number of petrol is to add high octane compounds like isooctane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether(MTBE). Out of these MTBE is preffered, because it contains oxygen in the form ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing the extent of peroxy compound formation

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"Unleaded petrol" is one where in the enhancement of octane rating is accomplished without the addition of lead compounds. It may be pointed here that a major advantage of unleaded petrol is that it permits the use of catalytic converter attached to the automobile exhaust.

Catalytic converter: [Auto mobile exhaust]

A catalytic converter contains a catalyst *Rh* (rhodium), which converts the toxic gases (CO and NO) to harmless gases (CO_2 and N_2 respectively). Moreover, it oxidises unburnt hydrocarbon into CO_2 and H_2O.

Gaseous Fuels:- Natural gas is the primary gaseous fuel. A variety of secondary fuels are obtained from coal or petroleum. They include coal gas, producer gas($CO+N_2+H_2$), water gas($CO+H_2O$) derived from coal. LPG (liquid petroleum gas) and CNG (compressed natural gas) are derived from natural gas and oil gas is formed by cracking of kerosene oil.

Natural gas:- Natural gas is obtained from oil wells dug in the oil bearing regions. When natural gas occurs along with lower hydrocarbons like CH_4, C_2H_6, it is called "wet gas". The wet gas is treated to remove propane, propene, butane, butene, which are used as LPG.

On the other hand when the gas is associated with higher hydrocarbons along with CH_4, is called "dry gas". Before use, the natural gas is purified to remove objectionable ingredients such as water, dust grit, H_2S, CO_2, N_2 and heavier liquefiable hydrocarbons (propane, propene, butane, butene, etc.).

The approximate composition of natural gas is :

CH_4 = 70-90%; C_2H_6= 5-10%; H_2 = 3%; $CO+CO_2$ = rest.

The calorific value varies from 12.000 – 14,000 Kcal/m^3

Uses of Natural gas:-

(1) It is an excellent domestic fuel and can be conveyed over very large distances in pipelines.

(2) It has recently been used in the manufacture of a number of chemicals by synthetic processes.

(3) It is also used as raw material for the manufacture of carbon black and hydrogen.

(4) A synthetic protein (used as animal feed) is obtained by microbiological fermentation of methane (which is main constituent of Natural gas).

Compressed natural gas: - (CNG)

CNG is natural gas compressed to a high pressure of about 1,000 atmospheres. A steel cylinder containing 15kg of CNG contains about $2X10^4$L or 20 m^3 of natural gas at 1 atmospheric pressure. CNG is now being used as a substitute for petrol and diesel, since it is comparatively much less pollution causing fuel. During its combustion, no sulphur and nitrogen gases are evolved. Moreover, No carbon particles are ejected. Hence it is a better fuel than petrol or diesel for automobiles. However initial cost of engine designed to use CNG as a fuel is comparatively higher then that of engine designed to use petrol or diesel. In Delhi it is mandatory for all buses, taxis and auto to use CNG as fuel.

Advantages of CNG:-

(1) Due to higher temperature of ignition, CNG is better fuel than petrol and diesels and / hence it is a much safer fuel.

(2) Operating cost of CNG is less.

(3) It releases least pollutants like CO and unburnt hydrocarbons.

(4) The conversion of gasoline operated automobiles into CNG operated vehicle is very easy.

(5) It undergoes regular combustion.

(6) No anti knocking agent is required as it has high octane number.

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Liquid petroleum gas:- (LPG) or as a

LPG is obtained from natural gas a byproduct in refineries during cracking of heavy petroleum products. The main constituents of LPG are n-butane, isobutane, butylene and propane, with little or no propylene and ethane. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, HP gas, etc.

Advantage of LPG:-

(1) It has high calorific value 27,800 kcal/m^3. The calorific value of LPG is roughly 3 times higher than that of natural gas and 7 times that of coal gas.

(2) It gives less CO and least unburnt hydrocarbon. So it causes least pollution.

(3) It gives moderate heat which is very good for cooking.

(4) Its storage is simple and is colourless.

(5) It has tendency to mix with air easily.

(6) Its on burning gives no toxic gases though it is highly toxic.

(7) It neither gives smoke nor ash content.

(8) It is cheaper than gasoline and hence used as fuel into auto vehicles.

(9) Needs little care for maintenance purpose.

Uses: The largest use of LPG at present is as domestic fuel and industrial fuel. However, there is a increasing trend to use LPG as motor fuel.

Rocket Propellants: Not in syllabus

A rocket engine is a tube like missile which carries both the fuel and the oxidant, collectively referred to as propellant. The propellant is burnt in a combustion chambers and a hot jet of gases at a pressure of 300 kg/cm^2 and a temperature of 3000°c comes out through a small nozzle at a supersonic velocity. This act of pushing of the gases downwards produces an equal and opposite reaction (Newton's third law of motion) causing the rocket to move upward.

Rockets are used for signaling, carrying a life, hurling explosives at an enemy, putting space capsule into orbit, etc. Most rockets at present use chemical propellants.

The propulsive force or thrust is due to the momentum of gas and can be calculated as

$$F = \frac{m}{g} \cdot v + (P_e - P_a) A_e$$

where,

F = thrust

m = mass flow rate of the propellant gases in kg

g = acceleration due to gravity in 9.81m^2/sec