

Fuels and Combustion

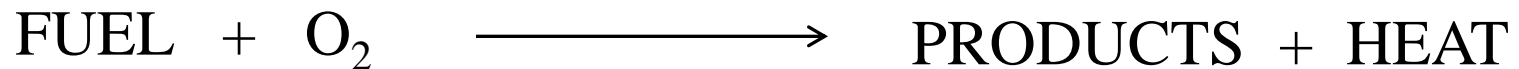
Dr. Sushil Kumar

Fuels

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

For example Wood, Charcoal, coal, Kerosene, petrol diesel, oil gas etc.

During the process of combustion of a fuel, the atom of carbon, hydrogen etc. combine with oxygen with simultaneous liberation of Heat at rapid rate. This energy is liberated due to the “rearrangement of valence electrons” in these atoms, resulting in the formation of Compounds like CO₂ and H₂O. These compounds have less energy (heat content) as compared to reactants.



More heat energy content

Lesser heat energy content

Classification of Fuels

These can be classified on the basis of their occurrence and physical state

On the basis of occurrence they are of two types:

Primary Fuels: Fuels which occur in nature as such are called primary fuels. E.g., wood, peat, coal, petroleum, and natural gas.

Secondary Fuels: The fuels which are derived from the primary fuels by further chemical processing are called secondary fuels. E.g., coke, charcoal, kerosene, coal gas, producer gas etc.

On the basis of physical state these may be classified as:

- Solid Fuels: woods, Peat, Lignite etc.
- Liquid Fuels: Crude oil, Tar, Diesel, Petrol, Kerosene. L.P.G.
- Gaseous Fuels: Natural gas, coal gas

Calorific value: It is defined as the total quantity of heat liberated when a unit mass (or volume) of a fuel is burnt completely.

Units of Calorific value:

System	Solid/Liquid Fuels	Gaseous Fuels
CGS	Calories/gm	Calories/cm ³
MKS	k cal/kg	k cal/m ³
B.T.U	BTU/lb	BTU/ft ³

The quantity of heat can be measured in the following units:

(i) Calorie: It is defined as the amount of heat required to raise the temperature of 1gm of water by 1°C

$$1 \text{ calorie} = 4.184 \text{ Joules}$$

(ii) Kilo Calorie: the quantity of heat required to raise the temperature of one kilogram of water by 1°C

$$1 \text{ k cal} = 1000 \text{ cal}$$

(iii) British thermal unit: (B. T. U.) It is defined as the amount of heat required to raise the temperature of 1 pound of water through 1°F.

$$1 \text{ B.T.U.} = 252 \text{ Cal} = 0.252 \text{ k cal}$$

(IV) Centigrade heat unit (C.H.U): It is defined as the amount of heat required to raise the temperature of 1 pound of water through 1°C.

$$1 \text{ k cal} = 3.968 \text{ B.T.U.}$$

$$= 2.2 \text{ C.H.U.}$$

Gross and net calorific Value

Gross Calorific Value: It is the total amount of heat generated when a unit quantity of fuel is completely burnt in oxygen and the products of combustion are cooled down to the room temperature.

As the products of combustion are cooled down to room temperature, the steam gets condensed into water and latent heat is evolved. Thus in the determination of gross calorific value, the latent heat also gets included in the measured heat. Therefore, gross calorific value is also called the higher calorific value.

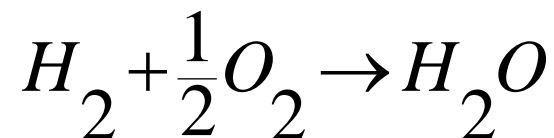
The calorific value which is determined by Bomb calorimeter gives the higher calorific value (HCV)

Net Calorific Value: It is defined as the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape.

The water vapour do not condense and escape with hot combustion gases. Hence, lesser amount than gross calorific value is available. It is also known as lower calorific value (LCV).

LCV=HCV-Latent heat of water vapours formed

Since 1 part by weight of hydrogen gives nine parts by weight of water i.e.



Therefore,

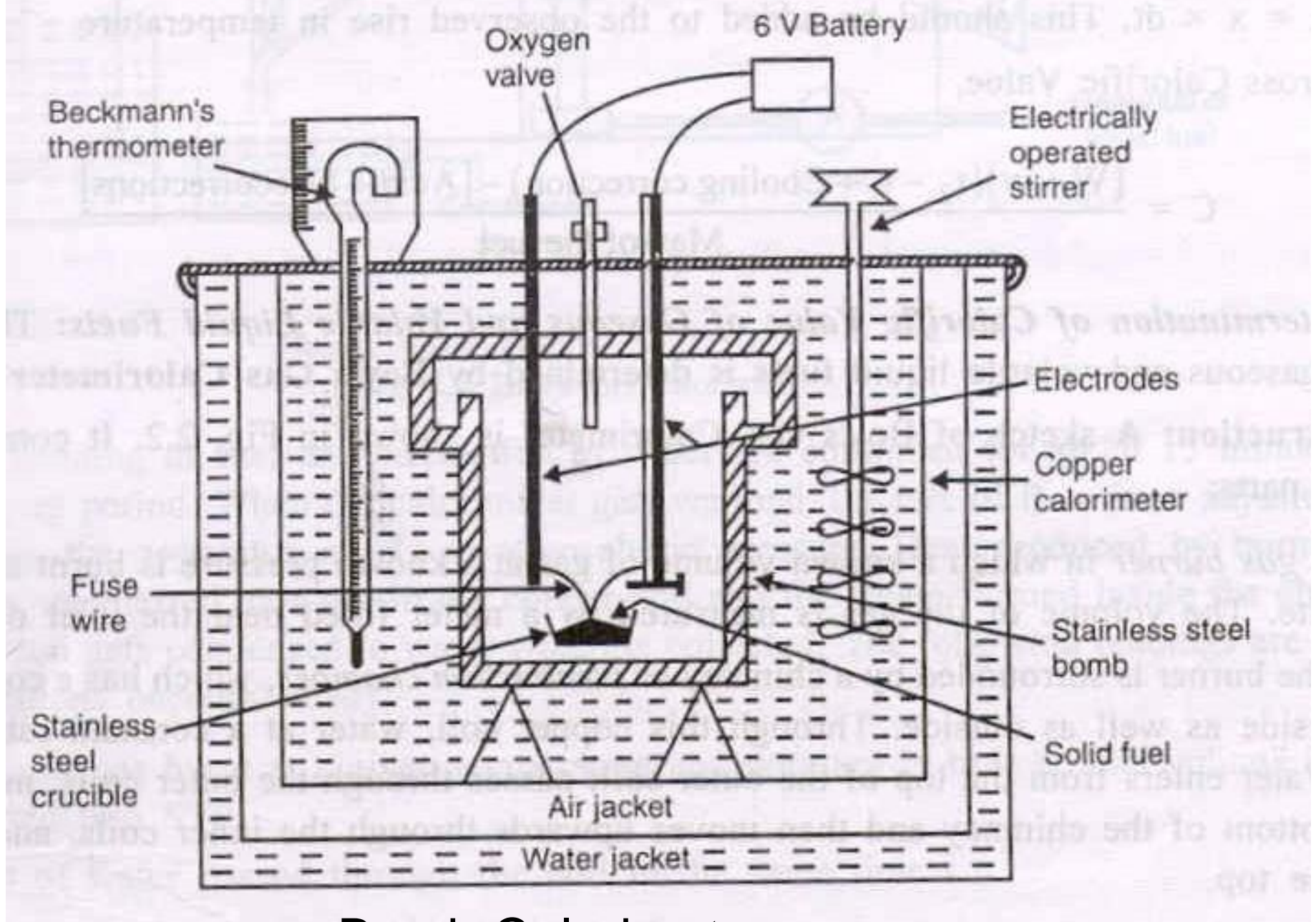
$\text{LCV} = \text{HCV} - \text{weight of hydrogen} \times 9 \times \text{latent heat of steam}$

$= \text{HCV} - \text{weight of hydrogen} \times 9 \times 587$

Determination of Calorific value

1. Determination of calorific value of solid and non volatile liquid fuels: It is determined by bomb calorimeter.

Principle: A known amount of the fuel is burnt in excess of oxygen and heat liberated is transferred to a known amount of water. The calorific value of the fuel is then determined by applying the principle of calorimetry i.e. Heat gained = Heat lost



Bomb Calorimeter

Calculations

Let weight of the fuel sample taken = x g

Weight of water in the calorimeter = W g

Water equivalent of the Calorimeter, stirrer, bomb, thermometer
= w g

Initial temperature of water = $t_1^\circ\text{C}$

Final temperature of water = $t_2^\circ\text{C}$

Specific heat of water = S

Higher or gross calorific value = C cal/g

Heat gained by water = $W \times \Delta t \times S$

$$= W (t_2 - t_1) S$$

Heat gained by Calorimeter = $w (t_2 - t_1) S$

Heat liberated by the fuel = $x C$ cal

Heat liberated by the fuel = Heat gained by water and calorimeter

$$x C = (W + w) (t_2 - t_1) S \text{ cal}$$

$$C = \frac{(W + w)(t_2 - t_1) S}{x} \text{ cal/g}$$

Note: the water equivalent of calorimeter is determined by burning a fuel of known calorific value and using above equation. The fuel used for this Purpose is benzoic acid (HCV = 6,325 kcal/kg) and naphthalene (HCV = 9,688 kcal/kg)

Net Calorific value:

Let percentage of hydrogen in the fuel = H

Weight of water produced from 1 gm of the fuel = $9H/100$ gm

Heat liberated during condensation of steam

$$= 0.09H \times 587 \text{ cal}$$

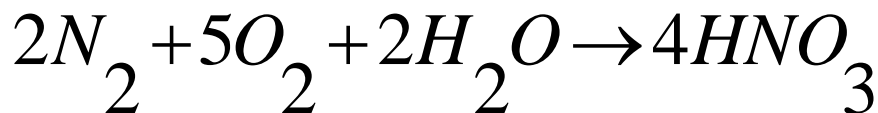
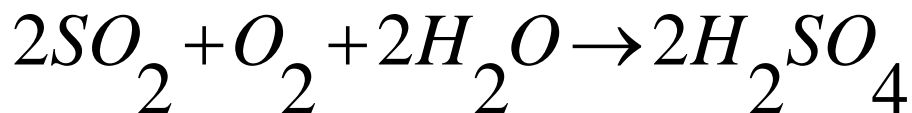
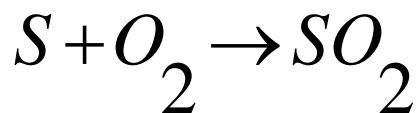
Net (Lower calorific value) = GCV-Latent heat of water formed

$$= C - 0.09H \times 587 \text{ cal/gm}$$

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

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

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



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

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

For each ml of 0.1 HNO_3 formed, 1.43 calories must be subtracted.

(C) Cooling correction: As the temperature rises above the room temperature, the loss of heat does occur due to radiation, and the highest temperature recorded will be slightly less than that obtained. A temperature correction is therefore necessary to get the correct rise in temperature.

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

Therefore, **Gross calorific value**

$$C = \frac{(W+w)(t_2-t_1) + \text{cooling correction} - [\text{Acid+fuse correction}]}{\text{Mass of Fuel}}$$

Some problems

Q:1 0.72 gram of a fuel containing 80% carbon, when burnt in a bomb calorimeter, Increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250 gm of water and its water equivalent is 150 grms, calculate the HCV of the fuel.

Give your answer in Kj/Kg.

Solution: here X=0.72 g, W=250 g; w=150g; t₁= 27.3°C; t₂=29.1°C

$$\begin{aligned}\text{HCV} &= (W+w)(t_2-t_1)/X \text{ Kcal/Kg} \\ &= (250+150)(29.1-27.3)/0.72 \\ &= 1,000 \text{ kcal/Kg} \\ &= 1,000 \times 4.2 \text{ KJ/Kg} \\ &= 4200 \text{ KJ/Kg}\end{aligned}$$

Some problems

On burning 0.83 gram of a solid fuel in a bomb calorimeter, the temperature of 3500 g water increase from 26.5°C to 29.2°C . water equivalent of calorimeter and latent heat of steam is 385 g and 587 cal/g respectively. If fuel contain 0.7% hydrogen, calculate the gross and net Calorific value

Some problems

A sample of coal contain c = 93%, H= 6% and ash = 1%. The following Data were obtained when the above coal was tested in bomb calorimeter

Weight of coal burnt = 0.92 g

Weight of water taken = 550 g

Water equivalent of bomb calorimeter = 2200 g

Rise in temperature = 2.42 °C

Fuse wire correction = 10 cal

Acid correction = 50 cal

Calculate gross and net calorific value. Assuming that latent heat of vapor is 580 cal/g.

Some problems

The following data is obtained in a bomb calorimeter

Weight of crucible = 3.649 g

Weight of crucible and fuel = 4.678 g

Water equivalent of bomb calorimeter = 570 g

Rise in temperature = 2.3 °C

Fuse wire correction = 3.6 cal

Acid correction = 3.8 cal

Cooling correction = 0.047 °C

Calculate gross and net calorific value if the fuel contain 6.5% hydrogen.

Some problems

Determine the water equivalent of the bomb calorimeter apparatus which gave the following data in the experiments

Weight of Benzoic acid = 1.346 g

Weight of calorimeter = 1025 g

Weight of calorimeter and water = 3025 g

Initial temperature = 11.872 °C

Final Temperature = 14.625 °C

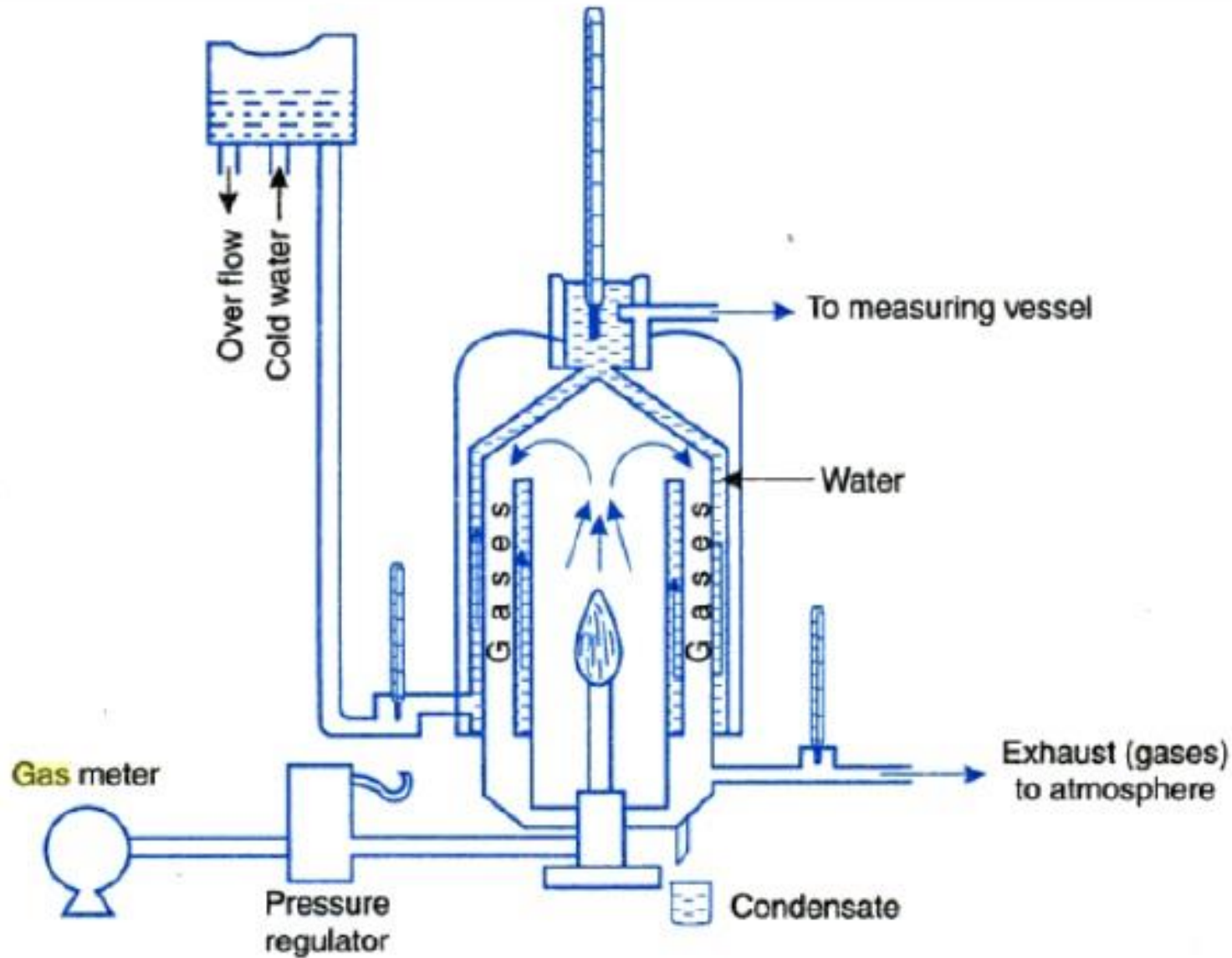
Cooling correction = 0.015 °C

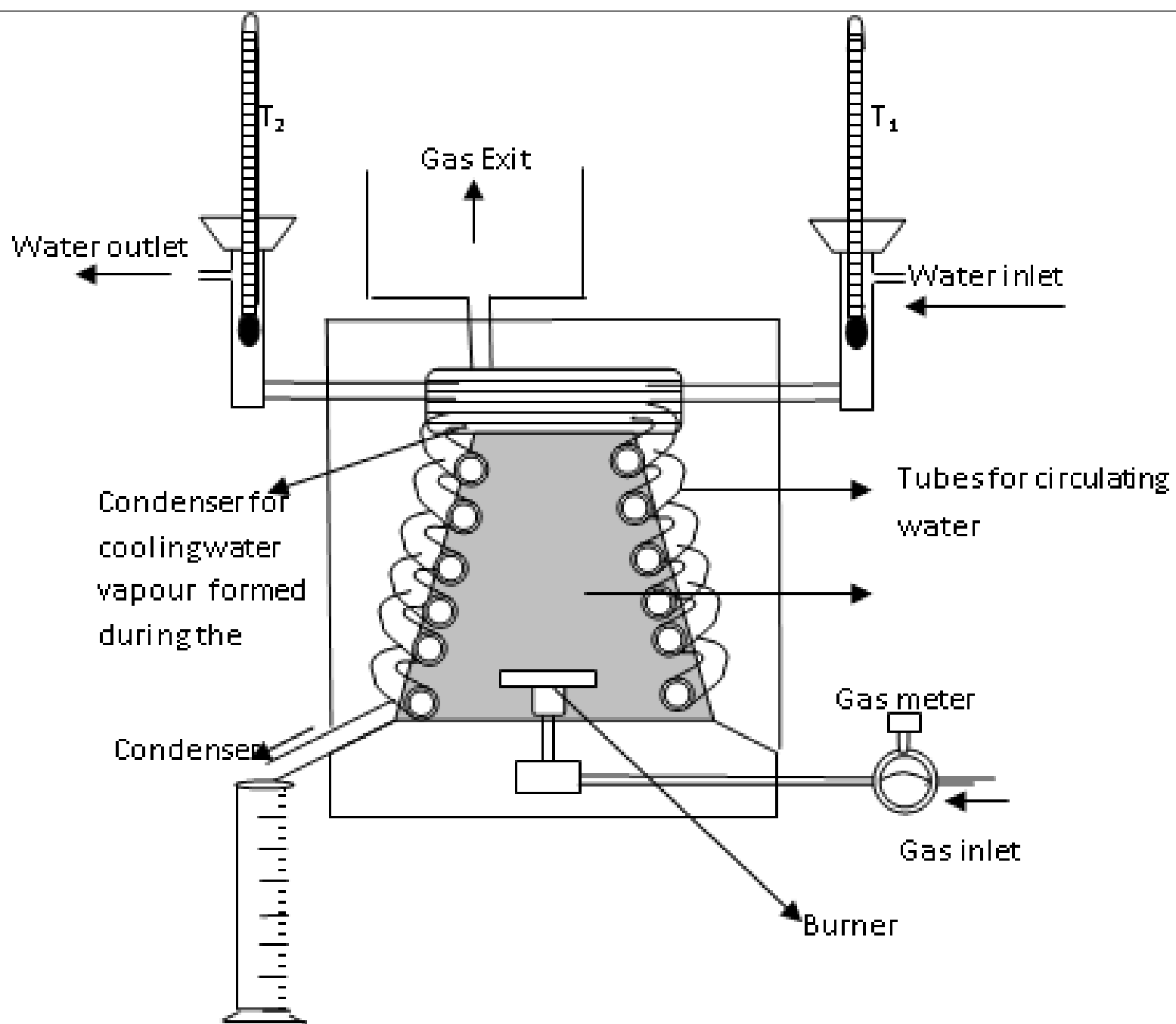
Heat from fuses = 22 cal

Calorific value of benzoic acid = 6324 cal/g

BOYS OR JUNKERS GAS CALORIMETER

AIM :To determine calorific value of gaseous fuel by Junkers gas calorimeter





BOYS OR JUNKERS GAS CALORIMETER

- **AIM :** To determine calorific value of gaseous fuel by Junkers gas calorimeter
- **APPARATUS:** It consists of following
 - (i) **Bunsen Burner:** special type of Burner clamped at the bottom. It can be pulled out of the combustion chamber or pushed up in chamber during the carrying out combustion.
 - (ii) **Gasometer:** It is employed to measure the volume of gas burning per unit time. This attached with manometer fitted with the thermometer so that pressure and temperature of the gas before burning can be read.
 - (iii) **Pressure governor:** It can control the supply of quantity of gas at give pressure.
 - (iv) **Gas Calorimeter/ Combustion chamber:** It is a vertical cylinder, which is surrounded by annular space for heating water and interchange coils. The entire is covered by an outer jacket in order to reduce the heat loss by radiation and convection.

PROCEDURE:

- Install the equipment on a flat rigid platform near an uninterrupted continuous water source of 1/2" size and a drain pipe.
- Connect the gas source to the pressure regulator, gas flow meter and the burner respectively in series
- Insert the thermometer / temperature sensors, into their respective places to measure water inlet and outlet temperatures and a thermometer to measure the flue gas temperature at the flue gas outlet
- Start the water flow through the calorimeter at a study constant flow rate and allow it to drain through over flow.
- Start the gas flow slowly and light the burner out side the calorimeter

When the steady condition are established, then the reading are taken simultaneously of:

- The volume of gaseous fuel burnt (V) at given temperature and pressure in certain period of time (t).
- The quantity of water (W Kg) passing through the annular space during the same interval of time
- The steady rise in temperature ($T_2 - T_1$)
- The mass of water (steam) condensed (in Kg) in the outlet water.

Calculation:

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

Mass of the cooling water used in time t = W

Temperature of inlet water = T_1

Temperature of outlet water = T_2

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

Higher calorific value of fuel = L

Specific heat of water = S

Heat absorbed by circulating water = $W(T_2 - T_1) \times \text{Specific heat of water (s)}$

Heat produced by combustion of fuel = VL

Thus

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

$$\text{HCV (L)} = W(T_2 - T_1) \times S / V$$

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

$$\text{LCV} = \left[L - \frac{m \times 587}{V} \right] \text{Kcal/m}^3$$

1 cm³ of water = 1 g of water

problems

The following were obtained in the Boy's gas calorimeter experiments

Volume of gas used = 0.1 m^3 at NTP

Weight of water heated = 25 Kg

Temp. of inlet water = 20°C

Temp. of outlet water = 33°C

Weight of steam condensed = 0.025 kg

Calculate the gross and net calorific value per m^3 at NTP. Take the heat liberated in condensing water is 580 Kcal/Kg

Some problems

During the determination of calorific value of a gaseous fuel by Boy's Calorimeter. The following results are obtained

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

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

Weight of steam condensed = 0.031 kg

Temp. of inlet water = 26.1°C

Temp. of outlet water = 36.5°C

Determine the gross and net calorific value of the gaseous fuel per cubic meter at NTP provided that the heat liberated in condensation of water

Vapor is 587 cal/g

problems

Calculate the gross calorific value and net calorific value of a gaseous fuel, 0.012m^3 of which when burnt raised the temperature of 3.5kg of water by 8.2K . Specific heat of water is $4.2\text{ kJ kg}^{-1}\text{K}^{-1}$. Latent heat of steam is 2.45 kJ kg^{-1} . The volume of water collected is 6.5cm^3 .

V = volume of the gas burnt	$= 0.015\text{ m}^3$
W = mass of water	$= 3.5\text{ kg}$
$t_2 - t_1$ = rise in temperature	$= 15.6\text{ K}$
s = specific heat of water	$= 4.2\text{kJ kg}^{-1}\text{K}^{-1}$
v = volume of water collected	$= 6.5\text{ cm}^3$

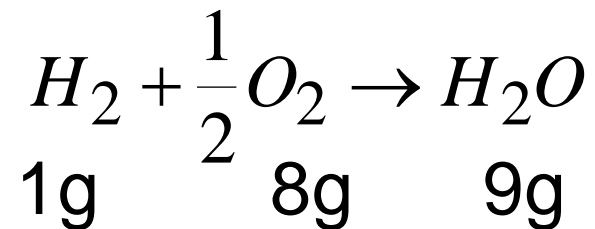
Theoretical calculation of Calorific value of a

Fuel: The calorific value of a fuel can be calculated if the percentages of the constituent elements are known.

Substrate	Calorific value (Kcal/kg)
Carbon	8080
Hydrogen	34500
Sulphur	2240

If oxygen is also present, it combines with hydrogen to form H_2O . Thus the hydrogen in the combined form is not available for combustion and is called fixed hydrogen.

Amount of hydrogen available for combustion = Total mass of hydrogen-hydrogen combined with oxygen.



Fixed Hydrogen = Mass of oxygen in the fuel

Therefore, mass of hydrogen available for combustion
= Total mass of hydrogen-1/8 mass of oxygen in fuel

= $H - O/8$

Dulong's formula for calculating the calorific value is given as:

Gross calorific Value (HCV)

$$= \frac{1}{100} [8080C + 34,500(H - \frac{O}{8}) + 2,240S] \text{ kcal / kg}$$

Net Calorific value (LCV)

$$\begin{aligned} &= [HCV - \frac{9H}{100} \times 587] \text{ kcal / kg} \\ &= [HCV - 0.09H \times 587] \text{ kcal / kg} \end{aligned}$$

Calculate the gross and net calorific value of coal having the following composition carbon = 85%, hydrogen = 8%, sulphur = 1%, nitrogen = 2%, Ash = 4 %, latent heat of steam 587cal/g.

Characteristics of Good Fuel:

- (i) **Suitability:** The fuel selected should be most suitable for the process. E.g., coke made out of bituminous coal is most suitable for blast furnace.
- (ii) High Calorific value
- (iii) **Ignition Temperature:** A good fuel should have moderate ignition temperature.
- (iv) **Moisture content:** Should be low
- (v) Non combustible matter content
- (vi) **Velocity of combustion:** It should be moderate
- (vii) Nature of the products
- (viii) Cost of fuel, (ix) Smoke, (x) Control of the process

Solid Fuels:

Wood: Wood has been used as a fuel from ancient times. Due to large scale deforestation, wood is no longer used.

- Freshly cut wood contains 25-50% moisture.
- Air dried wood contains about 10-15% moisture content.
- The calorific value of air dried wood is about 3500-4500 kcal/kg.
- When wood burns, the ash content is low but the oxygen content is very high. This makes even dry wood a fuel of low calorific value.
- Wood charcoal is obtained by destructive distillation of wood.
- The major use of wood charcoal is for producing activated carbon.

Coal: coal is highly carbonaceous fossil fuel that has been produced as a result of vegetable debris under favorable conditions of high temperature and pressure over million of years. It is chiefly composed of C, H, N and O besides non-combustible inorganic matter.

The transformation of the vegetable debris to coal takes place in two stages:

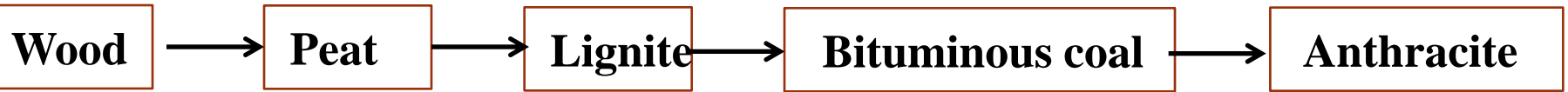
(a) Biochemical or peat stage: During this stage, the plant materials were attacked by various micro organisms.

(b) Chemical stage or metamorphism: In this stage, the peat deposit buried under sedimentary deposits lose moisture and volatile components under the effect of high temperature and pressure.

The peat gets enriched in carbon whereas its oxygen content decreases.

Classification of Coal: Coals are mainly classified on the basis of their degree of coalification from the parent material, wood. When wood is converted into coal, there is gradual increase in the concentration of carbon and decrease in the percentage of oxygen and nitrogen.

Coal is given a ranking depending upon the carbon content of the coal from wood to anthracite.



————— **Increase in carbon contents, Calorific value and hardness** —————>

————— **Decrease in H, O, S, N, contents and volatile matter** —————>

Type of coal	Percentage (dry, mineral matter free basis)					% moist ure	calorific value
	C	H	O	N	VM		
Wood	45-50	5-6	20-40	0-0.5	-	70-90	4000-4500
↓ Peat	45-60	3.5-6.5	20-45	0.75-3	45-75	70-90	4125-5280
↓ Brown Coal	60-75	4.5-5.5	17-35	0.75-2	45-60	30-50	6600-7100
↓ Bituminous coal	75-90	4.0-5.5	20-30	0.75-2	11-50	10-20	6600-8800
↓ Anthracite	90-95	3-4	2-3	0.5-2	3.8-10	1.5-3.5	8470-8800

Selection of coal

- ✓ **Calorific value** should be high
- ✓ **Moisture content** should be low
- ✓ **Ash content** should be low
- ✓ **Sulphur and phosphorus contents** of coal should be low
- ✓ **Size of coal** should be uniform

Analysis of Coal

In order to assess the quality of coal, the following two types of analysis are made:

- 1. Proximate analysis**
- 2. Ultimate analysis**

The results of analysis are generally reported in the following ways:

As received basis

Air dried basis

Moisture free basis (oven dried)

Proximate Analysis

Proximate analysis of coal determines the moisture, ash, volatile matter and fixed carbon of coal. It gives information about the practical utility of coal.

- 1. Moisture Content:** About 1 g of finely powered air dried coal sample is weighted in crucible. The crucible is placed in electric hot air oven, maintained at 105-110 °C. The crucible is allowed to remain in electric hot air oven for about one hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

Importance of Proximate analysis:

- Excess of moisture is undesirable in coal.
- Moisture lowers the calorific value of coal because it takes away appreciable amount of the liberated heat in the form of latent heat of vaporization.
- Excessive surface moisture may cause difficulty in handling the coal.
- Presence of excessive moisture quenches fire in the furnace.

2. Volatile Matter: It is determined by heating a known weight of moisture free coal sample in a covered platinum crucible with lid at $950 \pm 20^{\circ}\text{C}$ for 7 minutes in an electrical furnace. The crucible is cooled in a desiccator and weighed. Loss in weight is reported as volatile matter

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

Significance

- A high percent of volatile matter indicates that a large proportion of fuel is burnt as a gas.
- The high volatile content gives long flames, high smoke and relatively low heating values.
- For efficient use of fuel, the outgoing combustible gases have to be burnt by supplying secondary air.
- High volatile matter content is desirable in coal gas manufacture because volatile matter in a coal denotes the proportion of the coal which will be converted into gas and tar products by heat.

(3) Ash: Coal contains inorganic mineral substances which are converted into ash by chemical reactions during the combustion of coal. Ash usually consists of silica, alumina, iron oxide and small quantities of lime, magnesia etc.

Ash content is determined by heating the residue left after the removal of volatile matter at $700 \pm 50^{\circ}\text{C}$ for $\frac{1}{2}$ an hour without covering. The crucible is taken out, cooled first in air, then inside a desiccator and weighed. The residue is reported as ash on percentage basis.

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

Significance

The high percentage of ash is undesirable. It reduces the calorific value of coal.

In furnace grate, the ash may restrict the passage of air and lower the rate of combustion.

High ash leads to large heat losses and leads to formation of ash lumps.

The composition of ash and fusion range also influences the efficiency of coal.

(4) Fixed Carbon: The percentage of fixed carbon is given by:

Percentage of fixed carbon = $100 - [\% \text{ of moisture} + \text{volatile matter} + \text{ash}]$

Significance: Fixed carbon content increases from lignite to anthracite. Higher the percentage of fixed carbon greater is its calorific value and better is the quality of coal.

The percentage of fixed carbon helps in designing the furnace and shape of the fire-box because it is the fixed carbon that burns in the solid state.

Ultimate analysis: It is carried out to ascertain the composition of coal.

Ultimate analysis includes the estimation of carbon, hydrogen, sulphur, nitrogen and oxygen.

Carbon and Hydrogen: A known amount of coal is taken in a combustion tube and is burnt in excess of pure oxygen. C and H of coal are converted into CO_2 and H_2O respectively. These gaseous products are absorbed respectively in KOH and CaCl_2 tubes of known weight.

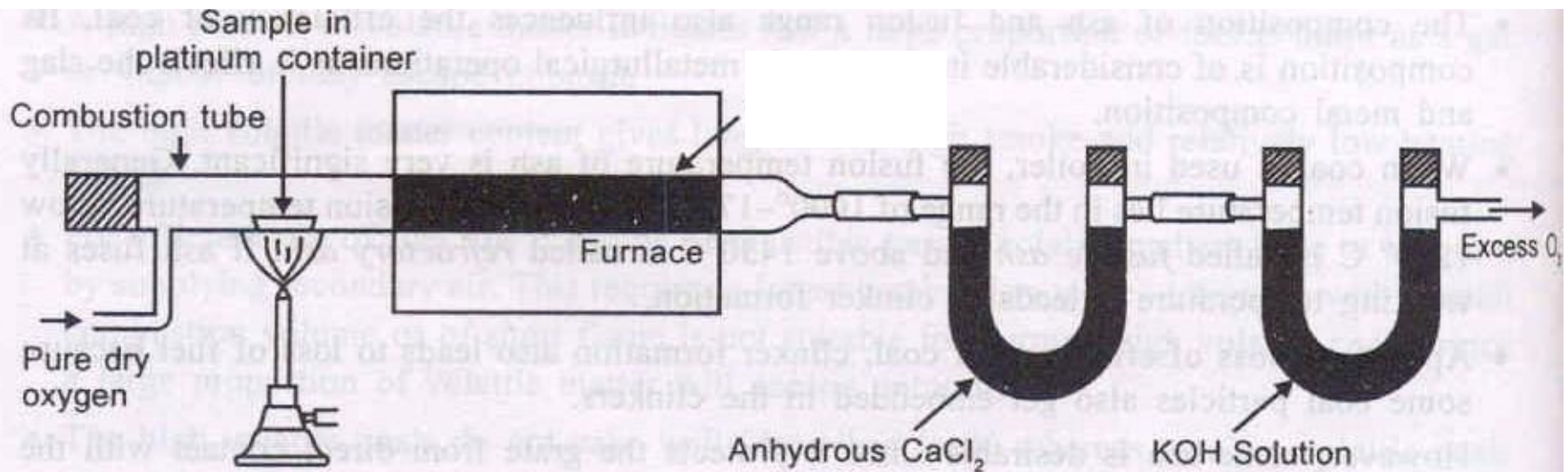
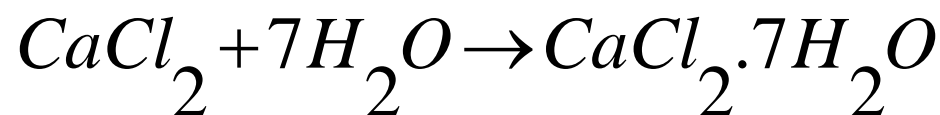
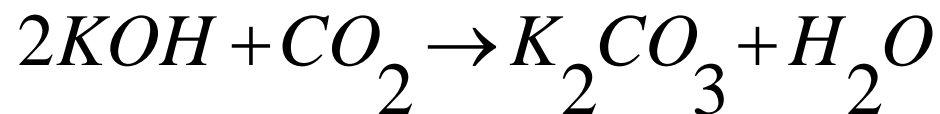
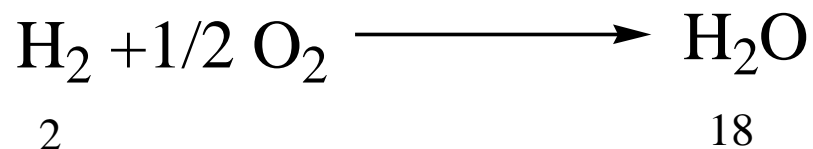
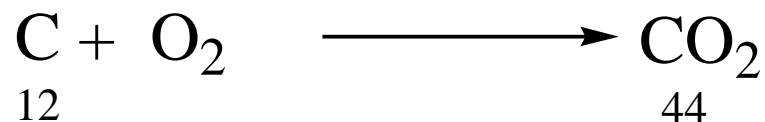


Fig. Estimation of carbon and hydrogen



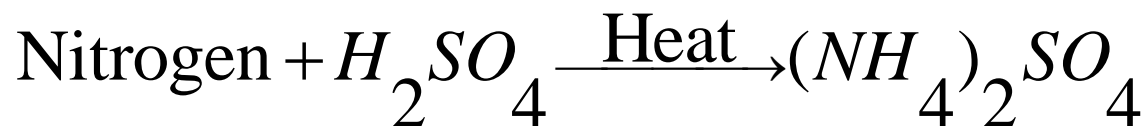
44 g of CO₂ contain = 12 g of carbon

Y g of CO₂ contain = $\frac{12}{44} \times Y$

Percentage of carbon = $\frac{12}{44} \times \frac{y \times 100}{\text{weight of coal taken}}$

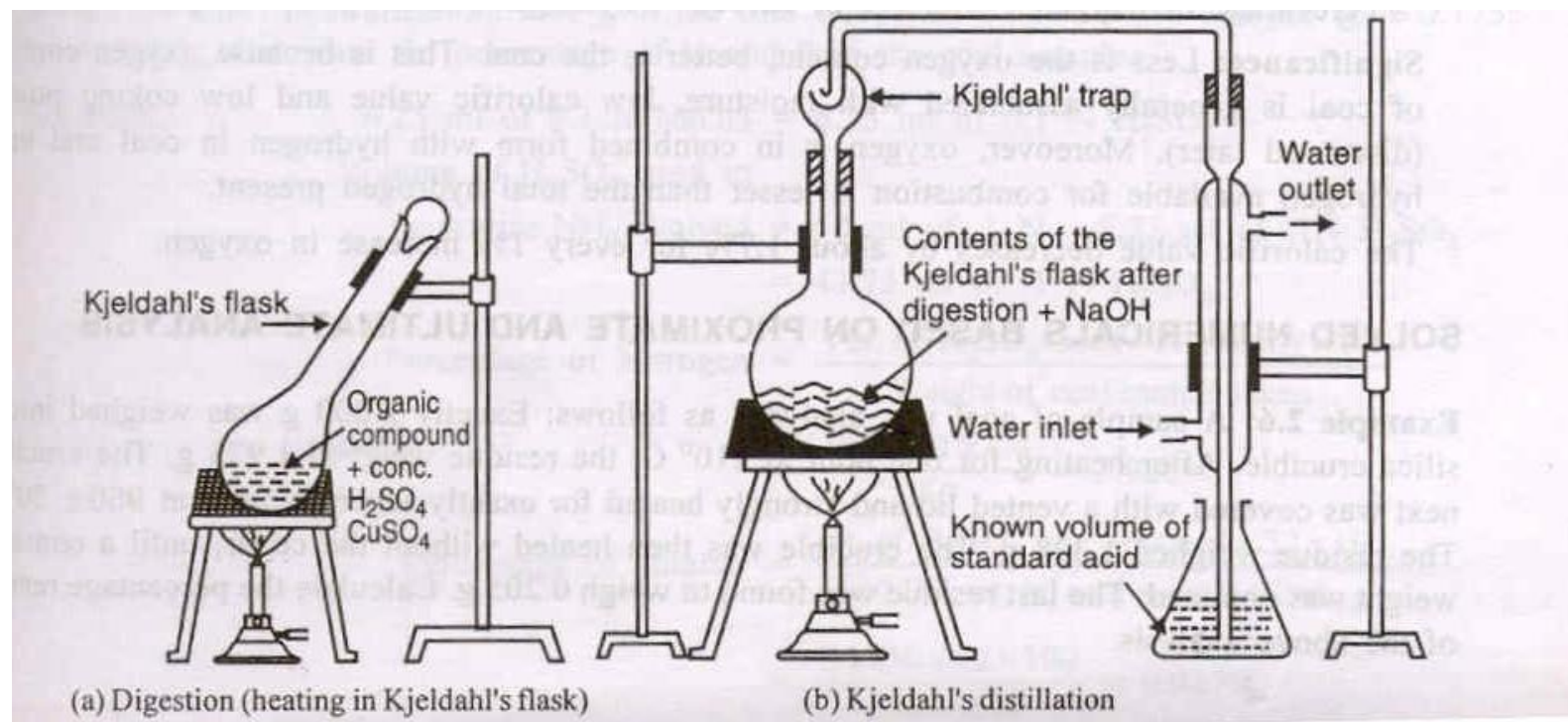
Percentage of hydrogen = $\frac{2}{18} \times \frac{z \times 100}{\text{weight of coal taken}}$

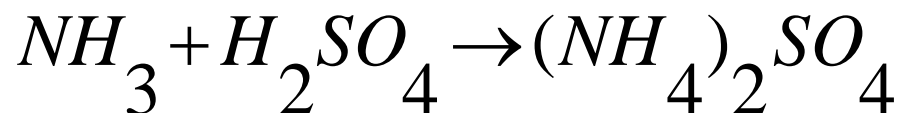
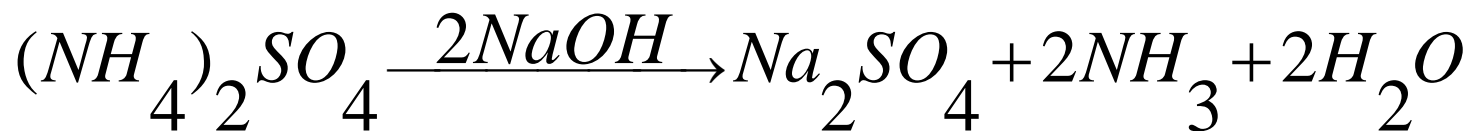
2. Nitrogen: Nitrogen present in coal sample can be estimated by Kjeldahl's method.



The contents are then transferred to a round bottomed flask and solution is heated with excess of NaOH.

The ammonia gas thus liberated is absorbed in a known volume of a standard solution of acid used.





The unused acid is then determined by titrating with NaOH. From the volume of acid used by NH_3 liberated, the percentage of nitrogen can be calculated.

(3) Sulfur is determined conveniently from the bomb washing from combustion of a known mass of coal in bomb calorimeter experiment. The washing contain Sulfur in the form of sulfate which it is precipitate as $BaSO_4$

$$\%S = \frac{\text{Weight of barium sulphate obtained} \times 32 \times 100}{\text{Weight of whole sample taken in bomb} \times 233}$$

(4) Ash is determined as described in proximate analysis

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

A sample of coal is analyzed as follows: Exactly 2.5 g was weighted into silica crucible. After heating for an hour at 110°C , the residue weighed 2.415g. The crucible next was covered with a vented lid and strongly heated For exactly seven minutes at 950°C . The residue weighed 1.528 g. the Crucible was then heated without the cover, until a constant weight was Obtained. The last residue was found to weight 0.245 g. calculate the percentage result of above analysis.

Liquid Fuels: The importance of liquid fuels is the fact that almost all combustion engines run on them.

Benefits of Liquid fuel:

- They are easy to handle, store and transport.
- After burning they do not leave any applicable amount of ash
- Liquid can easily kindled. The combustion can be started or stopped at once
- The rate of combustion can easily controlled as desired
- Less excess air is needed in case of liquid fuels as compare to solid fuel
- The furnace space is required is lesser than solid fuel
- Operation is cleaner

The largest source of liquid fuels is petroleum. The calorific value of petroleum is about 40000 kJ/kg. There are other supplements of liquid fuels such as coal tar, crude benzol, synthetic liquid fuel made from coal etc.

Petroleum: The term petroleum means rock oil. It is also called mineral oil.

Petroleum is a complex mixture of paraffinic, olefinic and aromatic hydrocarbons with small quantities of organic compounds containing oxygen, nitrogen and sulphur.

Composition:

Carbon = 79.5% to 87.1%

Hydrogen = 11.5% to 14.8%

Sulphur = 0.1% to 3.5%

Nitrogen and oxygen = 0.1% to 0.5%

Sulphur is present in the form of derivatives of hydrocarbons such as alkylsulphides, aromatic sulphides etc. Nitrogen is present in the form of pyridine, quinoline derivatives, pyrrole etc. Combined oxygen is present as carboxylic acids, ketones and phenols.

The ash of the crude oil is 0.1%. Metals e.g., Silicon, iron, aluminium, calcium, magnesium, nickel and sodium.

Classification of crude petroleum:

(1) Paraffinic base type crude oil:

These category of oil is mainly composed of saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ and little of naphthalene and aromatics. The hydrocarbon from $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{35}\text{H}_{72}$ are semi solids called waxes.

(2) Asphaltic Base type crude oil:

these category of oil contains mainly cycloparaffinis, or naphthalene with smaller amount of paraffinis and aromatic hydrocarbons.

(3) Mixed-based type crude oil:

these category of oil contains both paraffinic and asphaltic Hydrocarbons and are generally rich in semi solid waxes.

Processing of Crude Petroleum:

Petroleum is found deep below the earth crust. The oil is found floating over salt water or brine. Generally, accumulation of natural gas occurs above the oil.

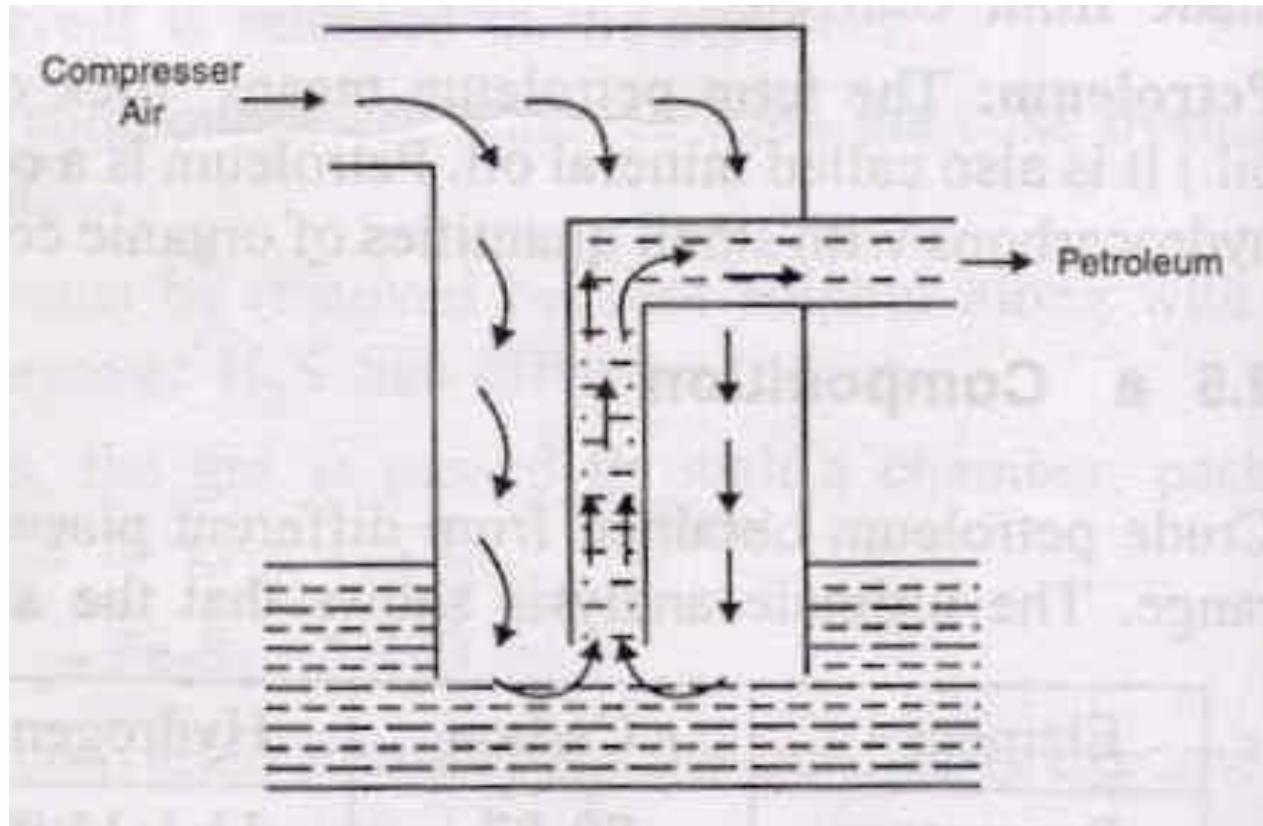


Fig. : Pumping of oil

Refining of Petroleum

Crude oil reaching the surface, generally consists of a mixture of solid, liquid and gaseous hydrocarbons containing sand and water. After the removal of dirt, water and much of the associated natural gas, the crude oil is separated into a number of useful fractions by fractional distillation and finally converted into desired specific products. The process of refining involves the following steps

Step 1: Separation of water (Demulsification): The crude oil coming out from the well, is in the form of stable emulsion of oil and salt water, which is yellow to dark brown in color. The demulsification is achieved by Cottrell's process, in which the water is removed from the oil by electrical process. The crude oil is subjected to an electrical field, when droplets of colloidal water coalesce to form large drops which separate out from the oil.

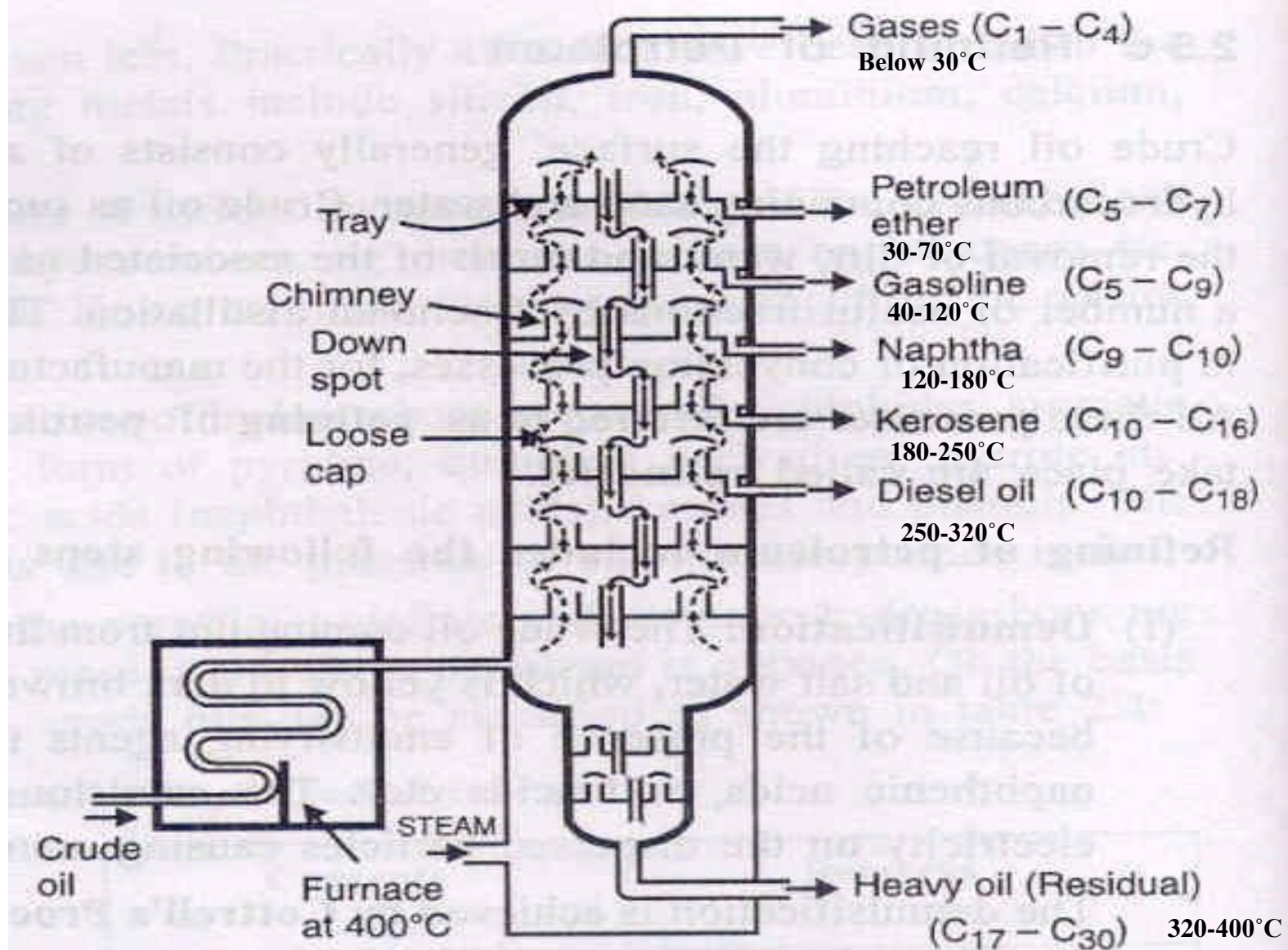
Step 2: Removal of harmful impurities: Excessive salt content such as NaCl and MgCl_2 can corrode the refining equipment. These are removed by washing with water. The objectionable sulphur compound are removed by treating the oil with copper oxide. The copper sulphide (solid) so formed is separated by filtration

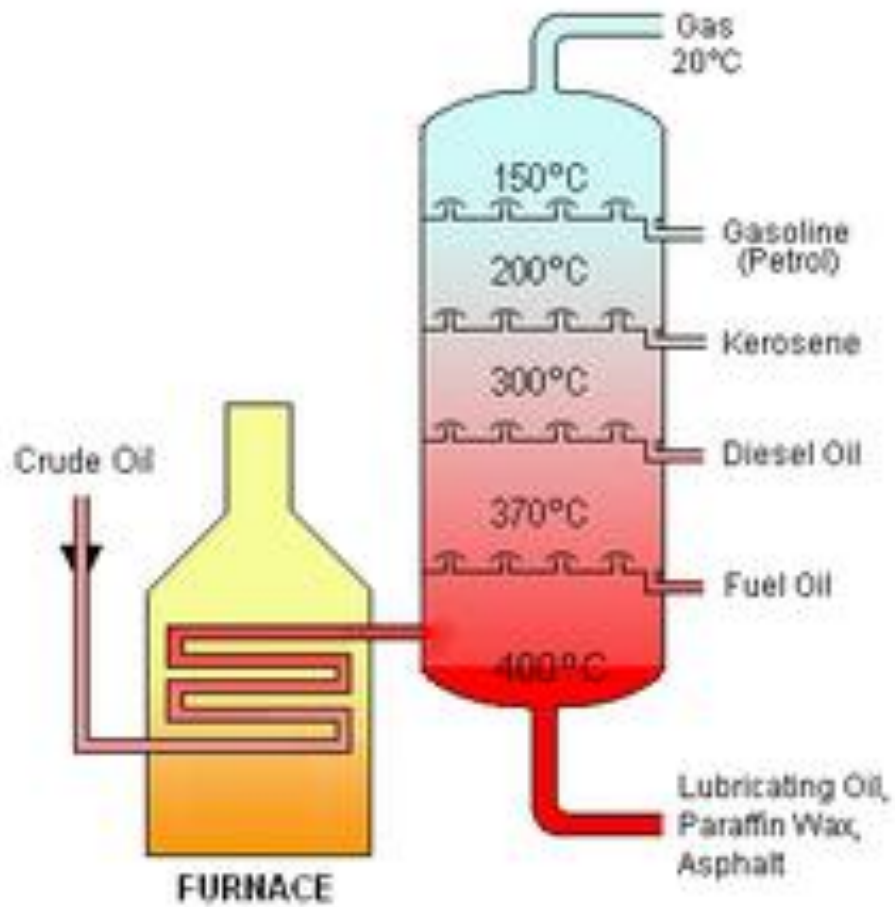
(iii) Fractional distillation is the separation of a mixture into its component or fractions on the basis of their boiling point by heating them to a temperature at which one or more fractions of the compound will vaporize.

It is done in tall fractionating tower or column made up of steel. Fractional column consists of horizontal trays provided with a no of small chimneys, through which vapors rise. These chimneys are covered with loose caps, known as bubble caps. These bubble caps help to provide an intimate contact between the escaping vapors and down coming liquid.

The temperature in the fractionating tower decreases gradually on moving upwards.

As the vapours of the crude oil go up, they become gradually cooler and fractional condensation takes place at different heights of column.





The residue from the bottom of the fractionating tower is vacuum distilled to recover various fractions

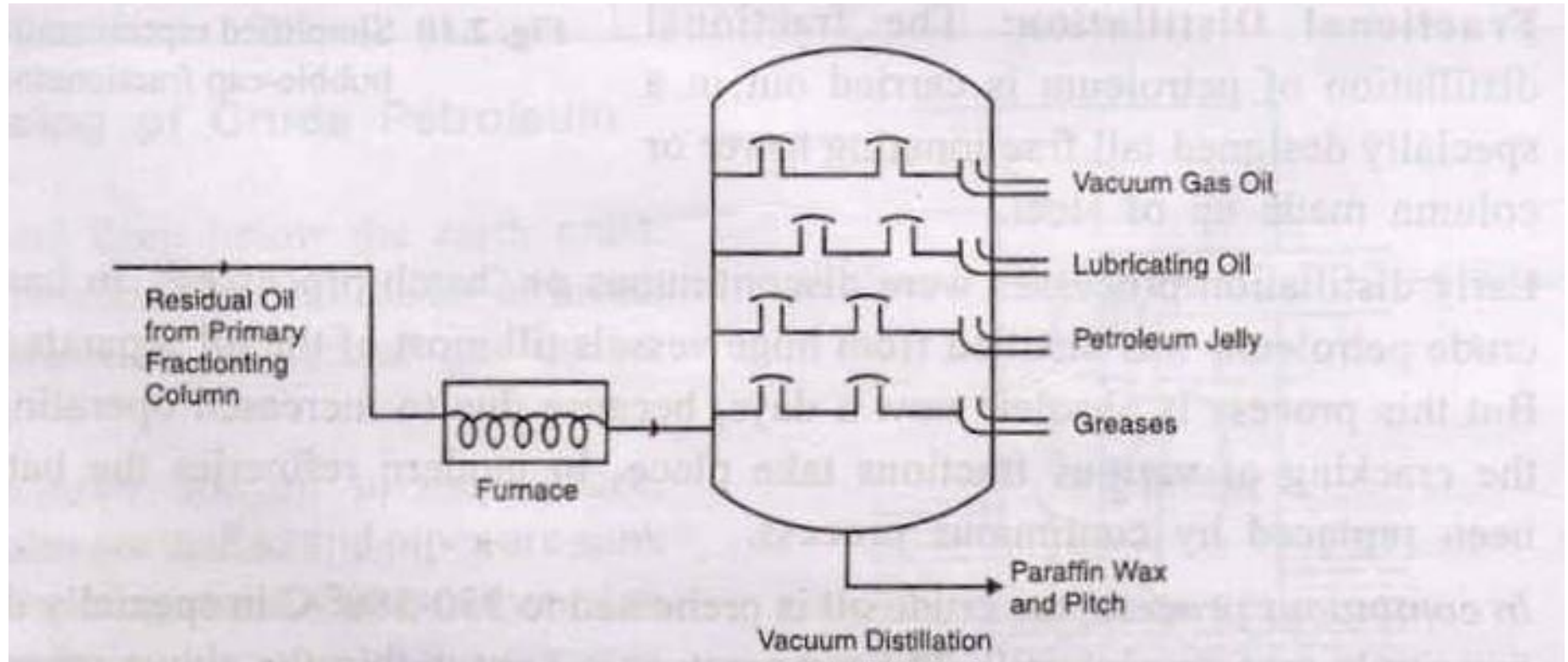
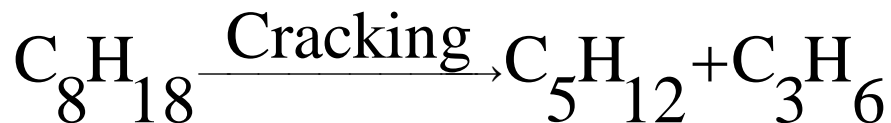
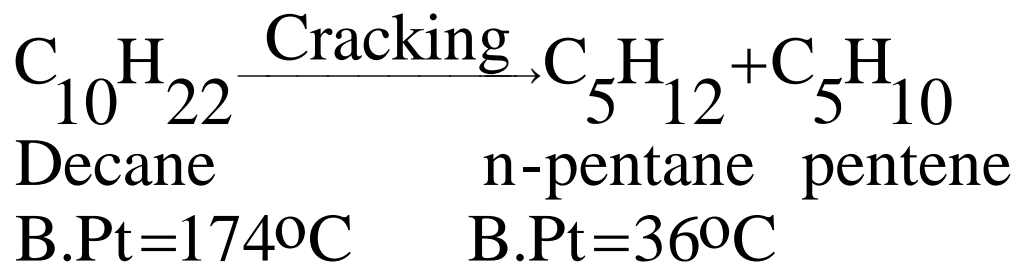


Fig. 11: Vacuum distillation of residual oil

Cracking

Gasoline (petrol) is the most important fraction of crude petroleum. The yield of this fraction is only 20% of the crude oil. The yield of heavier petroleum fraction is quite high. Therefore, heavier fractions are converted into more useful fraction, gasoline. This is achieved by a technique called cracking.

“Cracking is the process by which heavier fractions are converted into lighter fractions by the application of heat, with or without catalyst. Cracking involves the rupture of C-C and C-H bonds in the chains of high molecular weight hydrocarbons.”



Nearly 50% of today's gasoline is obtained by cracking. The gasoline obtained by cracking is far more superior than straight run gasoline.

The process of cracking involves the full chemical changes:

- Higher hydrocarbons are converted to lower
- Hydrocarbons by C-C cleavage. The product obtained on cracking have low boiling points than initial reactant.
- Formation of branched chain hydrocarbons takes place from straight chain alkanes.
- Unsaturated hydrocarbons are obtained from saturated hydrocarbons.
- Cyclization may takes place.
- Cracking can also be used for the production of olefins from naphtha's, oil gas from kerosene.

Cracking can be carried out by two methods

Thermal Cracking: The heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbons break down to give smaller molecules of paraffins, olefins etc. this process can be carried either *liquid phase* or *vapour phase*

- (a) Liquid Phase thermal cracking:** The heavy oil is cracked at a suitable temperature **475-530°C** and under pressures of the range **30-100 kg/cm²**. The cracked products are then separated in a fractionating column. The important fractions are: Cracked gasoline (30-35%), Cracking gases (10-45%); Cracked fuel oil (50-55%).
- (b) Vapour phase thermal cracking:** by this methods, only those oils can be cracked which vapourised at low temperature. The cracking oil is first vapourised and then cracked at about **600-650°C** and under a low pressures of **10-20 kg/cm²**.

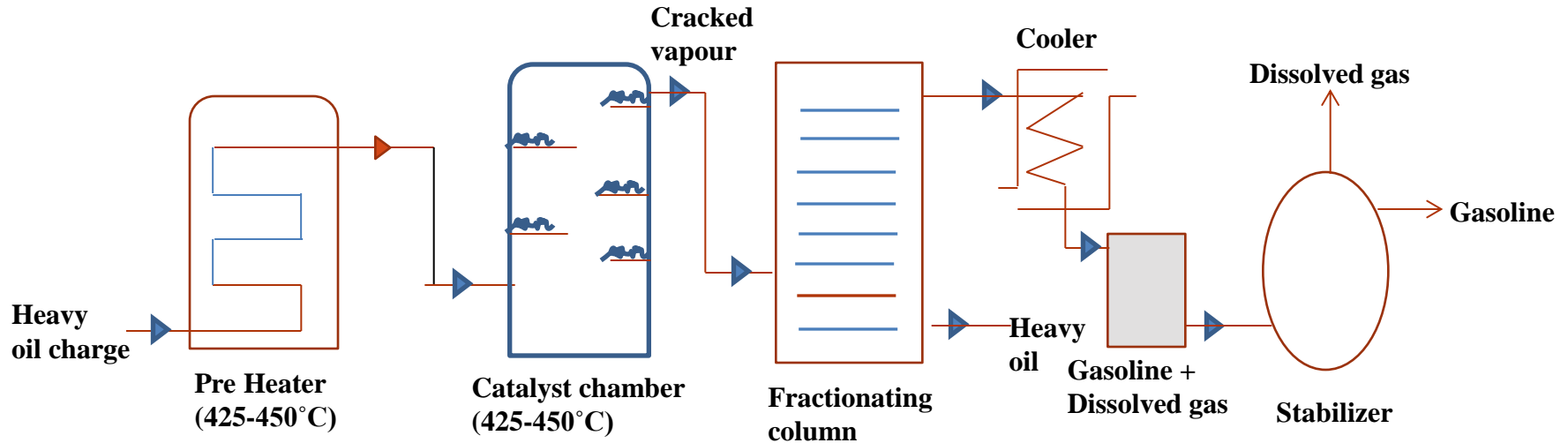
Catalytic cracking: Cracking is brought about in the presence of a catalyst at much lower temperatures and pressures. The catalyst used is mainly a mixture of silica and alumina. Most recent catalyst used is zeolite. The quality and yield of gasoline is greatly improved by this method.

Advantages of catalytic cracking over thermal cracking:

- High temp and pressure are not required in the presence of a catalyst.
- The use of catalyst not only accelerates the cracking reactions but also introduces new reactions which considerably modify the yield and the nature of the products.
- The yield of the gasoline is higher.
- The process can be better controlled so desired products can be obtained.
- The product contains a very little amount of undesirable sulphur because a major portion of it escapes out as H_2S gas, during cracking.
- It yields less coke, less gas and more liquid products.
- The evolution of by-product gas can be further minimized, thereby increasing the yield of desired product.
- Catalysts are selective in action and hence cracking of only high boiling fractions takes place.

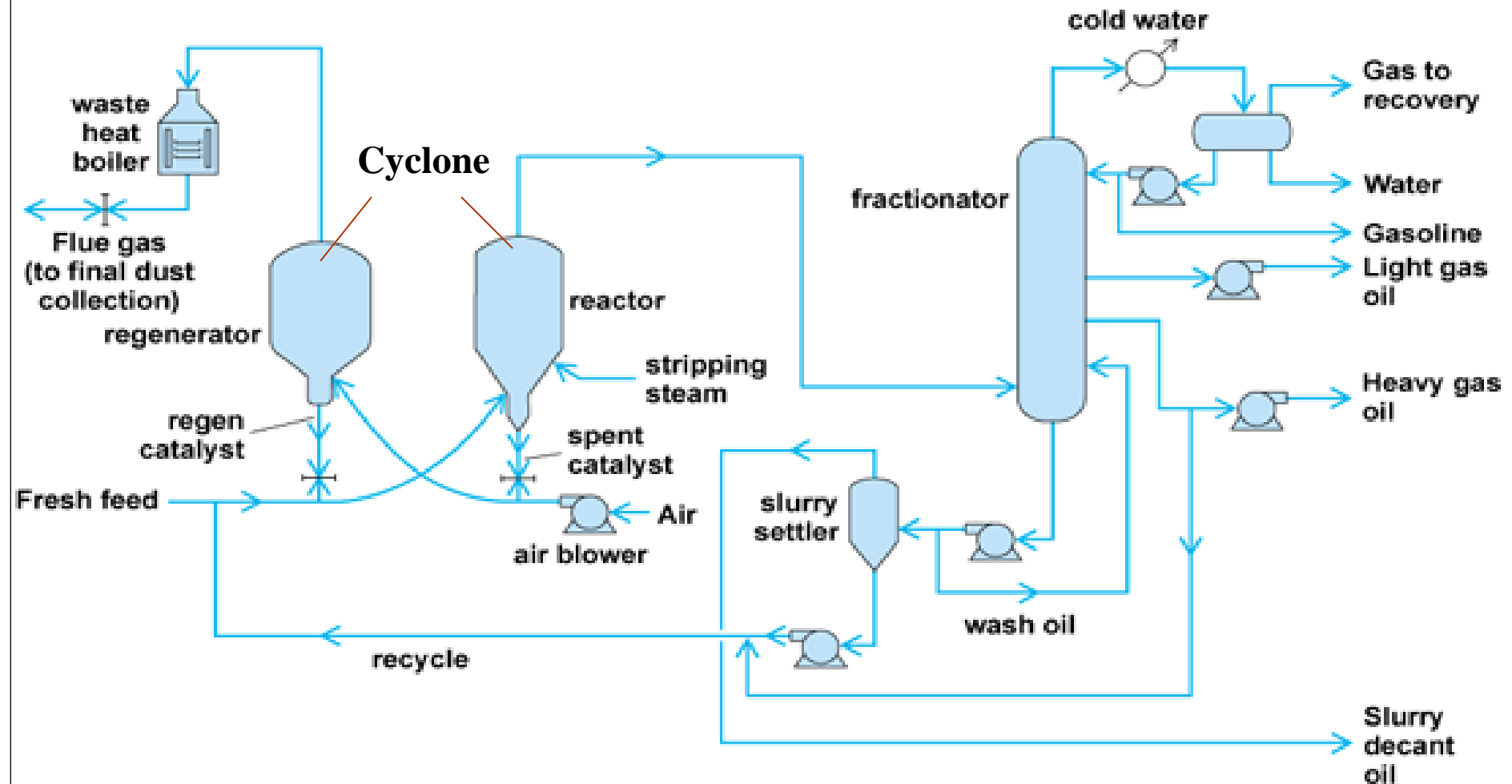
There are two methods for catalytic cracking:

(a) Fixed bed catalytic cracking:



The heavy oil are heated in a pre heater to cracking temperature (425-450°C) and then forced through the catalytic chamber (containing artificial clay and mixed with zirconium Oxide or silica-alumina gel) maintained at 425-450°C and 1.5 Kg/cm² pressure. During their passage through the tower about 40% heavy oil converted into gasoline and about 2-4% carbon formed. The vapour produced then passes through fractionating column, where heavy oil fraction condensed. The vapour are then led through a cooler, where some of the gas are condensed along with the gasoline and uncondensed gas move on. The gasoline containing gas is then sent to stabilizer, where the dissolved gas are removed and pur gasoline are obtained

(b) Moving-bed catalytic cracking:



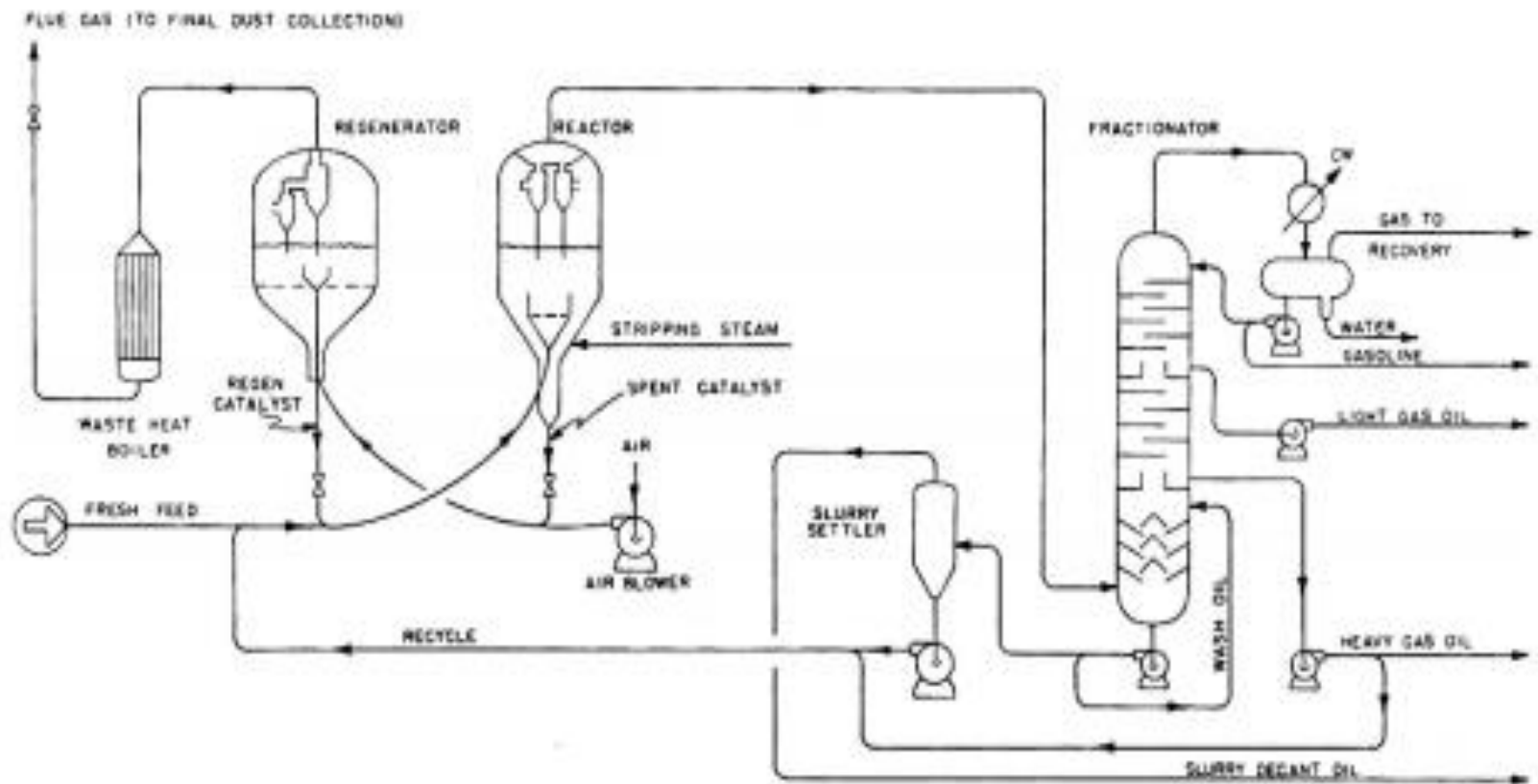


Figure 6.3 FCC unit, Model III.

Procedure:

- (1) The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which can be circulated in a gas stream.
- (2) The vapours of cracking stocks mixed with fluidized catalyst are forced up into a large reactor in which heavier molecules are cracked into lighter molecules. Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself.
- (3) The catalyst powder gradually becomes heavier, due to coating with carbon and settles to the bottom from where it is forced by an air blast to the regenerator (maintained 600°C).
- (4) In the regenerator, carbon is burnt and the regenerated catalyst then flows through a stand pipe for mixing with a fresh batch of incoming cracking oil.
- (5) At the top of the regenerator, there is a separator, which permits only gases (CO_2 etc.) to pass out, but holds back catalyst.