

Applied Chemistry

Paper Code-BS-103

Unit I

Fuels: Classification and Characteristics of fuels, Calorific values, Comparison between solid, liquid and gaseous fuels, calorific values of fuels, determination of calorific values using Bomb calorimeter, Boy's calorimeter, theoretical calculation of calorific value using Dulong formula and numericals of Calorific values. Types of fuels: - Solid: Coal, proximate and ultimate analysis of coal and numericals, carbonisation of coal in Otto-Hoffman oven with recovery of by-products, metallurgical coke; Liquid: Petroleum products --- refining, cracking-thermal and catalytic, knocking characteristics, Octane and Cetane rating; Gaseous: Natural Gas (NG), CNG, LPG, Coal gas, Oil gas, Producer gas, Water gas; Combustion of fuels numericals.

Unit II

Phase rule: Terms used in Gibb's Phase rule, phase diagram and its applications for study of one-component systems: Water and Sulphur and two-component systems: Lead-Silver and Zinc-Magnesium. Polymers: Classification, functionality and their types; Plastics: Synthesis (reactions) and properties of Polyethylene Plastics (Addition polymers) ---low-density polyethene (LDPE), high-density polyethylene(HDPE), linear low density polyethylene(LLDPE) and ultra-high molecular weight polyethylene (UHMWPE); Vinyl Plastics (Condensation polymers) -Nylons, Phenol-formaldehyde resins(Bakelite) and Glyptal; Speciality Polymers: Engineering thermoplastics, Conducting polymers, Electroluminescent polymers, liquid crystalline polymers and biodegradable polymers.

Unit III

Water: Introduction, water quality standards, physical, chemical and biological characteristics; hardness of water, disadvantages of hardness, determination of hardness (EDTA method) and related numerical questions. Alkalinity and its determination; Boiler problems with hard water and their prevention: Scale and sludge formation, boiler corrosion, caustic embrittlement, priming and foaming, boiler water treatment –internal or in-situ: carbonate and phosphate conditioning, colloidal and Calgon conditioning; external treatment: (a) Lime soda process and related numericals (b) Zeolite process and numericals, (c) Ion-exchange process. Municipal water supply – its treatment and disinfection using break -point chlorination. Desalination, Reverse Osmosis, Electrodialysis and defluoridation of water.

Unit IV

Corrosion and its Control: Definition, effects, theory (mechanisms): dry/chemical, wet/electrochemical corrosion, Pilling-Bedworth ratio; Types of corrosion: Galvanic corrosion, Soil corrosion, Pitting corrosion, Concentration cell or Differential Aeration corrosion, Stress corrosion; Mechanism of rusting of iron, Passivity. Factors influencing corrosion; protective measures: galvanization, tinning, cathodic protection, sacrificial anodic protection; electroplating and prevention of corrosion through material selection and design.Green Technology and Green Chemistry Twelve Principles of Green Chemistry, Zero Waste Technology, Atom economy, Use of alternative feedstock, innocuous reagents, alternative solvents, designing alternative reaction methodology, minimising energy consumption. Nano Chemistry: Nanomaterials: Properties, synthesis and surface characterization techniques BET and TEM and applications.

UNIT-I

1. Fuels: Introduction

A fuel is a material that, either by nuclear reaction or combustion, generates useful energy. One of a fuel's key characteristics is its regulated release of energy, which may be used profitably for both industrial and residential applications. Typical examples of fuels include wood, coal, charcoal, gasoline, diesel, kerosene, producer gas, and oil gas. Chemical fuels are defined as fuels that burn to produce heat energy. The fuel's carbon, hydrogen, sulfur, and phosphorus react with oxygen during burning to release energy.



However, heat production from a fuel does not always require burning. Nuclei can also fuse or fission to release energy. Chemical fuels, often known as nuclear fuels, release energy that is significantly less than this energy. For instance, tritium, uranium, plutonium, etc.

1.1 Classification of fuel

Fuels can be classified on the basis:

- (I) Occurrence
- (II) Physical state

(I) Fuels can be divided into two categories based on their occurrence.

(a) Natural or primary fuels

These are present in nature and are utilized as such, either unprocessed or somewhat treated, without changing the fuel's chemical makeup. Another name for this is fossil fuels. Wood, peat, lignite, coal, oil, natural gas, and so forth are a few examples.

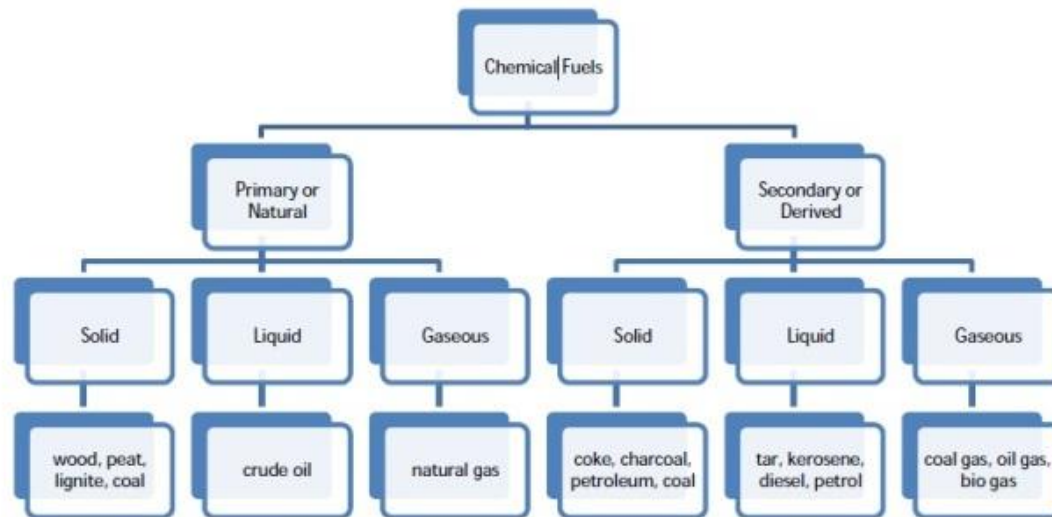
(b) Derived or secondary fuels

These fuels, such as coke, charcoal, kerosene, producer gas, water gas, etc., are obtained from primary fuels through additional chemical processing.

(II) Fuels can be categorized according to their physical state in the following ways:

- (a) Solid fuels
- (b) Liquid fuels
- (c) Gaseous fuels

The classification can be summarised as shown in the following diagram.



1.2 Characteristics of a Good Fuel

1. High Calorific Value

Since the calorific value of a fuel impacts its efficiency, a good fuel should have a high value. The amount of heat released per unit mass or volume increases with the calorific value.

2. Content of Moisture

Since moisture reduces the fuel's calorific value, the moisture content should be minimal.

3. Temperature of Ignition

It is the lowest temperature to which a fuel must be preheated so that it starts burning smoothly. An ideal fuel should have moderate ignition temperature. Low ignition temperature can cause fire hazards, making storage and transportation difficult. Fuel with low ignition temperature can burn spontaneously leading to explosion. High ignition temperature, on the other hand, makes it difficult to ignite the fuel.

4. Non-combustible Matter

The non-combustible material is left behind as ash or clinkers following combustion. In addition to lowering the fuel's calorific value, non-combustible matter raises the cost of managing, storing, and disposing of the waste products generated.

5. Velocity of Combustion

A low combustion velocity may cause some of the released heat to be radiated rather than increase the temperature, which could prevent the necessary high temperature from being reached. However, if the combustion velocity is extremely high, the rate of combustion may become uncontrollable. A moderate rate of combustion is required for fuel to provide a steady supply of heat.

6. Combustion Products

The fuel should burn to produce safe, non-polluting products. There should be less smoke produced and no harmful gasses such CO_2 , SO_2 , H_2S , PH_3 , and PbBr_2 .

7. Cost of the Fuel

A good fuel should be readily available at a low cost.

8. Combustion Should Be Controllable

The combustion process should be controllable, that is it can be started or stopped when required.

9. Storage and Transportation

A good fuel should be easy to handle, store and transport at low cost.

10. Size

For solid fuels, the size should be uniform to provide regular burning..

Comparison between solid, liquid and gaseous fuels

Solid fuels	Liquid fuels	Gaseous fuels
Combustible substances which are solid at room temperature are known as solid fuel	Volatile liquids which produce combustible vapours are known as liquid fuels.	Combustible gas or mixture of combustible gases is known as gaseous fuel.
produces a lot of residue when it burns.	No residue	No residue is left after burning.
Low calorific value.	Higher calorific value.	Higher calorific value than liquid and solid fuels.
High ignition temperature.	Low ignition temperature	Low ignition temperature
produce smoke, when it burns.	produce little or no smoke.	No smoke
cheap	costly	costly
Examples wood, coal, charcoal etc.	Examples petrol, kerosene, diesel etc.	Examples CNG, LPG, biogas, coal gas, water gas, producer gas and hydrogen gas.

2. Calorific Value

It is the total amount of heat released upon complete combustion of a unit mass or volume of fuel. It is measured in units such as cal/g or kcal/kg.

Units of heat

(i) Calorie It is defined as the amount of heat required to raise the temperature of 1 g of water by 1 °C (from 15 °C to 16 °C)

$$1 \text{ calorie} = 4.185 \text{ Joules} = 4.185 \times 10^7 \text{ ergs.}$$

(ii) Kilocalorie It is defined as the amount of heat required to raise the temperature of 1 kg of water by 1 °C (from 15 °C to 16 °C).

$$1 \text{ kcal} = 1000 \text{ cal.}$$

(iii) British Thermal Unit (BTU) It is defined as the amount of heat required to raise the temperature of 1 pound (lb) of water by 1 °F (from 60 °F to 61 °F)

$$1 \text{ BTU} = 252 \text{ cal} = 0.252 \text{ kcal} = 1054.6 \text{ Joule} = 1054.6 \times 10^7 \text{ ergs.}$$

(iv) Centigrade Heat Unit (CHU) It is defined as the amount of heat required to raise the temperature of one pound of water by 1 °C (from 15 °C to 16 °C).

$$1 \text{ kcal} = 3.968 \text{ BTU} = 2.2 \text{ CHU}$$

2.1 Units of calorific value

The units of calorific value for solid, liquid and gaseous fuels are given below.

Solid / Liquid fuels- calories/g(CGS), kcal/kg (MKS), BTU/lb (BTU)

Gaseous fuels- calories/cm³(CGS), kcal/m³(MKS), BTU/ft³(BTU)

These units can be interconverted as follows

$$1 \text{ cal/g} = 1 \text{ kcal/kg} = 1.8 \text{ BTU/lb}$$

$$1 \text{ kcal} = 0.1077 \text{ BTU/ft}^3$$

$$1 \text{ BTU/ft}^3 = 9.3 \text{ kcal/m}^3$$

2.2 Gross and Net Calorific Value

Gross Calorific Value (GCV) or higher calorific value(HCV)

It is defined as the total amount of heat produced when a unit quantity (mass/volume) of fuel is burnt completely, and the products of combustion are cooled to room temperature.

Hydrogen is typically present in all fuels. The fuel's hydrogen is transformed into steam during burning. When the combustion products are cooled to room temperature, the steam gets condensed into water and heat that equals the latent heat of condensation of steam is evolved. It is referred to as having a higher calorific value since this heat is included in the measured heat and hence has a high value.

Low Calorific Value (LCV) or Net calorific value (NCV)

It is defined as the heat produced when a unit quantity (mass/volume) of a fuel is burnt completely and the hot combustion products are allowed to escape. In reality, water vapor escapes with the hot combustion gases as a fuel burns, resulting in less heat being available than the gross calorific value. Thus, LCV or NCV is the term used to describe this.

Thus $LCV = HCV - \text{Latent heat of water vapour formed.}$

As 1 part by weight of hydrogen gives 9 parts by weight of water,



$$LCV = HCV - \text{Weight of hydrogen in unit mass/volume of fuel} \times 9 \times \text{latent heat of steam}$$

2.3 Determination of Calorific Value

The calorific value of solid and non-volatile liquid fuels is determined by bomb calorimeter, whereas the calorific value of gaseous fuels is determined by Junkers calorimeter.

2.3.1 Bomb calorimeter

Principle

The bomb calorimeter is referred to as an instrument which is mostly used for the purpose of measuring the heat of reaction that is found having a fixed volume in order to measure the heat which is also termed as the change of internal energy (ΔE). Chemically, the changes of heat reaction needs to be measured at fixed pressure or volume.

Heat liberated by fuel = Heat absorbed by water and the calorimeter.

Construction:

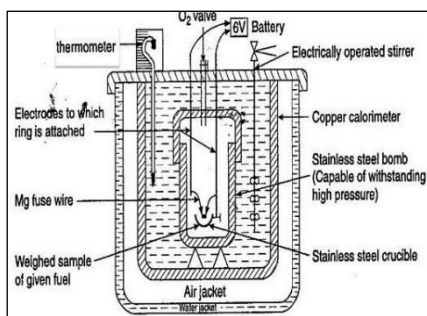


Fig. Bomb Calorimeter

It consists of the following parts:

(i) Stainless Steel Bomb

It consists of a long cylindrical container made up of stainless steel. It has a lid that is made air tight with the help of screws. The lid is provided with two holes for electrodes and has an oxygen inlet valve. A small ring is attached to one of the electrodes. This ring acts as a support for nickel or stainless steel crucible in which the fuel is burnt. Magnesium wire touching the fuel sample extends across the electrodes. The steel bomb is lined inside with platinum to resist corrosive action of HNO_3 and H_2SO_4 vapors formed because of burning of fuel and is designed to withstand high pressure (25–50 atm).

(ii) Copper Calorimeter

The bomb is placed in a copper calorimeter containing a known amount of water. The calorimeter is provided with an electrical stirrer and a Beckmann thermometer that can read accurate temperature difference of up to 1/100th of a degree.

(iii) Air Jacket and Water Jacket

The copper calorimeter is surrounded by an air jacket and a water jacket to prevent loss of heat owing to radiation.

Working

- A clean crucible that is supported over the ring is filled with a known quantity of fuel (0.5–1 g).
- After that, a thin magnesium wire is stretched between the electrodes, touching the fuel sample.
- The bomb's lid is screwed close after about 10 ml of distilled water is added to absorb sulfuric and nitric acid fumes produced during combustion.
- The bomb is filled with oxygen at 25 atm. and placed in the copper calorimeter containing a known weight of water.
- After starting the stirrer, the water's initial temperature is recorded.
- The electrodes are then connected to a 6-volt battery to complete the circuit.
- The sample burns and heat is liberated. This heat is absorbed by water.
- Maximum temperature shown by the thermometer is recorded.
- Time taken to cool the water in the calorimeter from maximum temperature to room temperature is also noted.

The gross calorific value of the fuel is calculated as follows.

Weight of fuel sample taken = x g

Weight of water in the calorimeter = W g

Water equivalent* of calorimeter,

stirrer, thermometer, bomb etc = w g

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

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

Higher calorific value of fuel = H calorie / g

Heat liberated by burning of fuel = $x \times H$

Heat gained by water = $W \times \Delta T \times \text{specific heat of water}$
 $= W (t_2 - t_1) \times 1 \text{ cal}$

Heat gained by calorimeter = $w (t_2 - t_1)$

Total heat gained = $W (t_2 - t_1) + w (t_2 - t_1)$
 $= (W + w) (t_2 - t_1)$

But Heat liberated by the fuel = Heat absorbed by water and calorimeter.

$$x \times H = (W + w) (t_2 - t_1)$$

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

Net (lower) calorific value

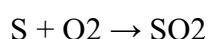
LCV = HCV – $0.09 H \times 587 \text{ cal/g}$ or kcal/kg

(Latent heat of condensation of steam = 587 kcal/kg).

The correction factors used to get accurate results include:

(a) Fuse Wire Correction The gross calorific value calculated above includes the heat liberated by the ignition of Mg fuse wire; 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 get oxidised to H_2SO_4 and HNO_3 , respectively:



The formation of acids is exothermic and this should be subtracted from the obtained value of GCV.

(c) Cooling Correction Heating and cooling occur at the same time. As the temperature rises above the room temperature, the loss of heat occurs due to radiation and the highest temperature recorded will be slightly less than that obtained if there was no heat loss. A temperature correction (cooling correction) is therefore necessary to get the correct rise in temperature.

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

$$\text{HCV of fuel (H)} = \frac{(W+w)(t_2-t_1+\text{cooling correction})-(\text{Acid}+\text{fuse wire correction})}{\text{Mass of the fuel (x)}}$$

2.3.2 Boy's Gas Calorimeter

This calorimeter is used to find the calorific value of gaseous and volatile liquid fuels. It consists of the following parts.

1. Gas Burner

A known volume of gas is burned at a known pressure using a gas burner. A gasometer is used to measure the amount of gas burned, and a pressure governor is used to track the gas's pressure.

2. Combustion Chamber

The combustion chamber or chimney has copper tubes coiled inside and outside the combustion chamber. Water circulates in these coils. It enters from the top of the outer coil, passes through the outer coils, moves to the bottom of the chimney and then moves upwards through the inner coil and exits from the top.

3. Thermometers

Two thermometers t_1 and t_2 measure the temperatures of the incoming and outgoing water.

4. Beaker

A graduated beaker is placed at the bottom to collect the condensed steam produced during combustion.

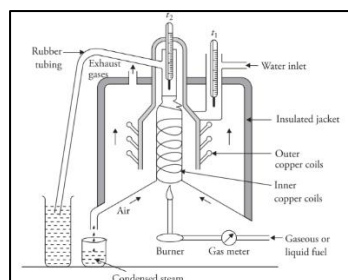


Fig. Boy's gas calorimeter

Working

- A known volume of gas is burnt at a constant rate in a combustion chamber in the presence of excess air.
- The water is circulated and the fuel is burnt to provide an initial warming period of 15 minutes.
- When the calorimeter is warmed, the rate of flow of the gas is adjusted and it is burnt inside the calorimeter.
- The heat produced by the combustion is absorbed by water circulating in the copper tubes.
- The rise in temperature, volume of gas burnt, volume of water circulated in the coils in time t and the mass of steam condensed help in finding the calorific value of the given fuel sample.

Observations

The volume of gaseous fuel burnt at a given temperature and pressure in a certain time = $V \text{ m}^3$

Weight of water circulated through the coils in time $t = W \text{ g}$

Temperature of inlet water = $t_1 \text{ }^\circ\text{C}$

Temperature of outlet water = $t_2 \text{ }^\circ\text{C}$

Weight of steam condensed in time t in a graduated cylinder = $m \text{ kg}$.

Let GCV of the fuel = H

Heat produced by the combustion of fuel = $V \times H$

Heat absorbed by circulating water = $W (t_2 - t_1)$

Assuming no loss of heat,

$$V \times H = W (t_2 - t_1)$$

HCV or GCV

$$H = \frac{W(t_2 - t_1)}{V} \text{ kcal/m}^3$$

Weight of steam condensed in a certain time t by the combustion of $V \text{ m}^3$ of the fuel = $m \text{ kg}$

Mass of H_2O condensed per m^3 of the fuel = $m/V \text{ kg}$

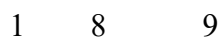
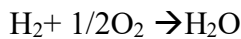
Latent heat of steam per m^3 of the fuel $= \frac{m \times 587}{V}$ kcal

therefore, NCV or LCV $= \left[H - \frac{m \times 587}{V} \right]$ kcal/ m^3

2.3.3 Theoretical Calculation of Calorific Value of a Fuel

Dulong's assumed that the heat evolved comes from the combustion of carbon, hydrogen and sulphur present in the fuel, and the calorific value of the fuel is the sum of the calorific values of these constituents. The calorific values of C, H and O are found to be 8080, 34500 and 2240 kcal/kg, respectively.

If oxygen is also present, it combines with hydrogen to form H_2O . Thus, the hydrogen in 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.



that is 8 parts of oxygen combines with 1 part of hydrogen to form water or for every 8 parts of oxygen, 1 part of hydrogen gets fixed.

If the fuel contains x mass of oxygen then

$$\text{Fixed hydrogen} = \frac{1}{8} \times x = \frac{\text{mass of oxygen in fuel}}{8}$$

$$\text{Amount of hydrogen available for combustion} = \left(H - \frac{O}{8} \right)$$

Dulong's formula for calculating calorific value is given as

$$\text{Gross calorific value (HCV)} = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S \right] \text{ kcal/kg}$$

Here C, H, O and S are percentages of carbon, hydrogen, oxygen and sulphur in fuel.

$$\text{Net calorific value (LCV)} = \left(\text{HCV} - \frac{9H}{100} \times 587 \right) \text{ kcal/kg}$$

$$(\text{HCV} - 0.09 H \times 587) \text{ kcal/kg}$$

(Latent heat of steam = 587 kcal/kg).

3. Solid Fuels

Solid fuel refers to various types of solid materials that are used as fuel to produce energy. The primary solid fuels commonly used are wood and coal.

Wood Wood is being used as fuel from times immemorial. Freshly cut wood contains 25 to 50% moisture which reduces to 15% after drying the wood in air.

The average composition of wood is:

$$C = 55\%$$

$$H = 6\%$$

$$O = 43\%$$

$$\text{ash} = 1\%$$

Its calorific value is about 3500–4500 kcal/kg. It burns with a long and non-smoky flame leaving behind small amount of ash. Destructive distillation of wood at around 500 °C produces charcoal which is an excellent fuel equivalent to the best of fuels.

Coal Coal is produced when the plant and animal debris are subjected to conditions of high temperature and pressure over millions of years. Hence, it is regarded as a fossil fuel. It chiefly comprises C, H, N and O besides non-combustible matter.

3.1 Coal - Classification

Classification of coal based on volatile matter and cooking power of clean material.

Coal is a readily combustible rock containing more than 50% by weight of carbonaceous material formed from compaction and indurations of variously altered plant remains similar to those in peat. After a considerable amount of time, heat, and burial pressure, it is metamorphosed from peat to lignite. Lignite is considered to be "immature" coal at this stage of development because it is still somewhat light in color and it remains soft.

- **Lignite** increases in maturity by becoming darker and harder and is then classified as sub-bituminous coal. After a continuous process of burial and alteration, chemical and physical changes occur until the coal is classified as bituminous - dark and hard coal.
- **Bituminous coal** ignites easily and burns long with a relatively long flame. If improperly fired bituminous coal is characterized with excess smoke and soot.
- **Anthracite coal** is the last classification, the ultimate maturation. Anthracite coal is very hard and shiny.

Typical Sulfur Content in Coal

- Anthracite Coal: 0.6 - 0.77 weight %
- Bituminous Coal: 0.7 - 4.0 weight %
- Lignite Coal: 0.4 weight %

Typical Moisture Content in Coal

- Anthracite Coal: 2.8 - 16.3 weight %
- Bituminous Coal: 2.2 - 15.9 weight %
- Lignite Coal: 39 weight %

Typical Fixed Carbon Content in Coal

- Anthracite Coal: 80.5 - 85.7 weight %
- Bituminous Coal: 44.9 - 78.2 weight %
- Lignite Coal: 31.4 weight %

Typical Density of Coal

- 1100 - 1800 (kg/m³)

Typical Bulk Density of Coal

- Anthracite Coal: 50 - 58 (lb/ft³), 800 - 929 (kg/m³)
- Bituminous Coal: 42 - 57 (lb/ft³), 673 - 913 (kg/m³)
- Lignite Coal: 40 - 54 (lb/ft³), 641 - 865 (kg/m³)

Typical Ash Content in Coal

- Anthracite Coal: 9.7 - 20.2 weight %
- Bituminous Coal: 3.3 - 11.7 weight %
- Lignite Coal: 4.2 weight %

3.2 Analysis of Coal

The composition of coal varies widely. It is necessary to analyse and interpret the results for the purpose of price fixation, commercial classification and proper industrial utilisation. The quality of coal is ascertained by two types of analysis:

- Proximate analysis
- Ultimate analysis

3.2.1 Proximate Analysis

It is an empirical but important analysis dealing with the determination of moisture content, volatile matter, ash content and fixed carbon. It is called proximate analysis because the data vary with the procedure adopted. This analysis provides data for a general assessment of the quality and type of coal. It involves the following determinations:

1. Moisture Content

A known weight of coal (air-dried) is taken in a crucible and heated in an electric hot air oven at about 105 °C–110 °C for about one hour. After 1 hour, it is taken out from the oven and cooled in a desiccator and weighed. Loss in weight of the sample is found out and the percentage of moisture is calculated as follows:

Let the weight of coal sample = W g

Weight after heating for 1 h = W_1 g

Loss in weight, that is the weight of moisture = $(W - W_1)$ g

$$\% \text{ Moisture} = \frac{(W - W_1)}{W} \times 100$$

$$= \frac{\text{Loss in weight of the sample or weight of moisture}}{\text{Weight of coal sample taken}} \times 100$$

Significance

- A high moisture content lowers the calorific value and raises the cost of transportation, which makes it undesirable.
- Presence of excessive moisture quenches fire in the furnace.
- A considerable amount of heat is wasted in evaporating the moisture during combustion.

2. Volatile Matter

The volatile matter present in the coal may be combustible gases such as H_2 , CO , CH_4 and other hydrocarbons or non-combustible gases such as CO_2 and N_2 . It does not include moisture of the coal. It is determined by heating a known weight of moisture-free coal in a silica crucible covered with a vented lid at 950 ± 20 °C for 7 minutes in a muffle furnace. The crucible is then taken out and cooled inside a desiccator and weighed again. Complete removal of volatile matter is judged by bubbling the gas through a water seal. Loss in weight gives the weight of the volatile matter and the percentage of volatile matter is calculated as follows:

Let the weight of sample after removal of volatile matter = W_2 g

Loss in weight, that is the weight of moisture = $(W_1 - W_2)$ g

$$\% \text{ Volatile matter} = \frac{(W_1 - W_2)}{W} \times 100$$

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

It may be noted here that it is not correct to say coal with 20% volatile matter or coal containing 20% volatile matter because volatile matter is not present as such in coal but it is the product of thermal

decomposition of coal; hence, it should be accurately described as coal yielding 20% volatile matter although the former term is widely used in coal analysis.

Significance

- Coal containing high percentage of volatile matter burns with a long flame and high smoke and has low calorific value. Coals with high percentage of volatile matter ignite easily but burn very quickly.
- A significant amount of volatile materials will escape unburned if the furnace capacity is small or the flame is short.
- Coals with higher percentage of volatile matter do not cake well, whereas medium volatile coals containing 20–30% of volatile matter are capable of forming hard and strong coke on carbonisation.
- Coals with low volatile matter do not cake at all, making them unsuitable for producing coke.
 - Because volatile matter in coal indicates the percentage of coal that will be heated into gas and tar products, high volatile matter is preferred in the production of coal gas.
 - However, for the manufacture of metallurgical coke, coal with low volatile matter content is preferred.

3. Ash

Ash is the non-combustible, useless matter that is left behind when all the combustible substances have burnt off from coal. Ash usually consists of silica, alumina, iron oxide and small quantities of lime, magnesia, etc.

Ash content is determined by heating the residue obtained after removal of moisture and volatile matter at 700 ± 50 °C for half an hour without a lid in muffle furnace. The residue left is cooled in a dessicator and weighed. The percentage of ash is calculated from the residue weight as

Let the weight of ash formed = W_3 g.

$$\% \text{ Ash} = \frac{W_3}{W} \times 100$$

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

Significance

- An excessive amount of ash is undesirable because it lowers the fuel's calorific value.
- Presence of ash increases the transporting, handling and storage cost.
- It also involves additional cost of ash disposal.
- Clinkers, or chunks of fused ash, obstruct the grate's interspaces when coal is burned. This causes obstruction in air supply. Hence, burning of coal becomes irregular. Hence, lower the ash content better the quality of the coal.

4. Fixed Carbon

Fixed carbon is the material remaining after determination of moisture, volatile matter and ash content. It is determined indirectly by the formula:

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

Significance

- The calorific value increases with the percentage of fixed carbon.
- Coals with high fixed carbon content are difficult to ignite but they burn slowly.

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

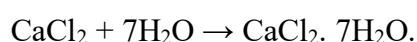
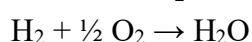
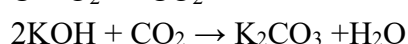
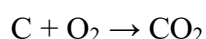
3.2.2 Ultimate Analysis

It is also called elemental analysis and is used for the determination of carbon, hydrogen, nitrogen, sulphur and oxygen. This analysis requires high degree of skill and the equipments are expensive. However, it gives exact results that are useful in calculating the calorific value of coal using *Dulong's formula*.

- **Carbon (C):** Main combustible element; higher carbon content generally increases the calorific value and quality of the coal.
- **Hydrogen (H):** Also contributes to the heating value and influences the flames' characteristics.
- **Nitrogen (N):** Has minimal effect on calorific value but can contribute to the formation of harmful nitrogen oxides during combustion.
 - **Sulfur (S):** Contributes to heating value but causes pollution and corrosion due to the formation of sulfur oxides upon combustion.
 - **Oxygen (O):** Usually determined by difference (100% - sum of other measured elements); does not contribute to calorific value and high oxygen indicates lower quality coal.
 - **Ash:** Inorganic residue left after complete combustion, representing the mineral content of coal.

1. Carbon and Hydrogen

Carbon in coal sample occurs in combined form in complex organic matter and can also be present as mineral carbonates. Hydrogen on the other hand is found in organic matter in coal and is also found associated with the moisture present in coal. To estimate carbon and hydrogen accurately weighed coal sample is burnt in a combustion tube in a current of O₂ (free from CO₂ and moisture). The carbon and hydrogen present in the fuel is converted to CO₂ and H₂O, respectively. These are then absorbed by previously weighed tubes containing KOH and anhydrous CaCl₂. The increase in weights of these tubes gives the amount of CO₂ and H₂O formed. The percentage of C and H is then calculated as follows:



Let the weight of coal sample taken = x g.

Increase in weight of KOH tube = y g.

Increase in weight of CaCl₂ tube = z g.

Now,

44 g of CO₂ contains 12 g of C

y g of CO₂ contains $\frac{12}{44} \times y$ g of C.

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{y}{x} \times 100$$

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

Similarly,

18 g of H₂O contains 2 g of H

z g of H₂O contains $\frac{2}{18} \times z$ g of C.

Percentage of Hydrogen = $\frac{2}{18} \times \frac{z}{x} \times 100$

or percentage of Hydrogen = $\frac{2}{18} \times \frac{\text{increase in weight of CaCl}_2 \text{ tube}}{\text{weight of coal sample taken}} \times 100$

Significance

- A fuel's calorific value is directly proportional to its carbon content; hence, the higher the fuel's carbon percentage, the higher its calorific value.
- Percentage of carbon increases from lignite to anthracite; thus, the percentage of carbon forms the basis of classification of coal.
- High percentage of hydrogen also increases the calorific value of coal. However, hydrogen is mostly associated with volatile matter and affects the use to which coal is put.
- In carbonisation and gasification industries, hydrogen of coal is responsible for the production of many useful materials such as gaseous hydrogen, methane, etc.

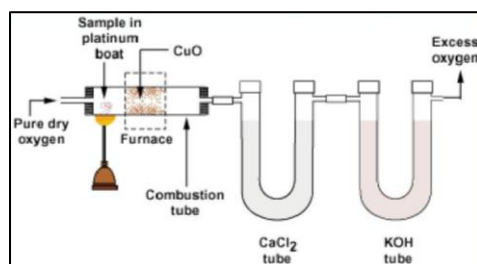
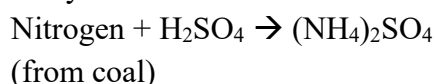


Fig. Determination of carbon and hydrogen

2. Nitrogen

All the nitrogen present in coal is assumed to occur within the organic matter of coal. Nitrogen present in coal sample is estimated by Kjehldahl's method.

- Accurately weighed coal sample is heated with concentrated H₂SO₄ in the presence of K₂SO₄ in a long-necked flask known as Kjehldahl's flask. Nitrogen present in the coal gets converted to (NH₄)₂SO₄ quantitatively.



When a clear solution is obtained (i.e., whole nitrogen is converted into ammonium sulphate), the contents are transferred into a round bottom flask and the solution is heated with excess of NaOH to liberate NH₃.

- The NH₃ thus liberated is absorbed in a known volume of a standard H₂SO₄ solution (N/10).

- The volume of unused H_2SO_4 is determined by titrating against standard NaOH solution (N/10). Difference gives the volume of acid used. From the volume of acid used by NH_3 , the percentage of nitrogen can be calculated.

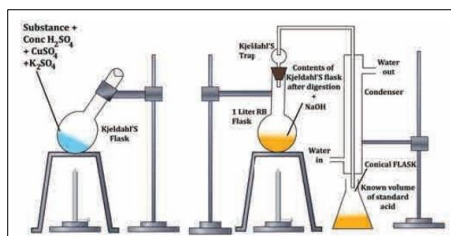
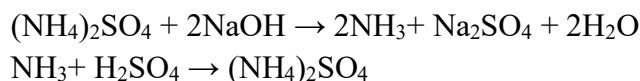


Fig. Estimation of nitrogen

Let the weight of coal taken = W g

Volume of acid used = V_1 mL

Normality of acid = N_1

As we know,

Equivalents of H_2SO_4 used = Equivalent of NH_3 formed

Equivalents of H_2SO_4 used = $N_1 V_1$

Hence, equivalents of NH_3 formed = $N_1 V_1$

Now,

Normal (1N solution of NH_3 means 1 g equivalent NH_3 dissolved in 1 liter water)

1000 mL contains 17 g NH_3 = 14 g nitrogen.

$N_1 V_1$ of NH_3 will contain $= \frac{14}{1000} \times N_1 V_1$ nitrogen

% Nitrogen = $\frac{14}{1000} \times \frac{N_1 V_1}{W} \times 100$

% Nitrogen = $\frac{1.4 \times \text{Normality of } \text{H}_2 \text{SO}_4 \times \text{Volume of } \text{H}_2 \text{SO}_4 \text{ used}}{\text{Weight of coal sample taken}}$

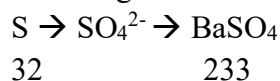
Significance

Since nitrogen is an inert and incombustible gas with no calorific value, its presence in fuel is undesirable.

3. Sulphur

Sulphur is found in coal in three forms, as organic sulphur compounds, as inorganic sulphides and also as inorganic sulphates. To estimate the amount of sulphur in the coal sample a known amount of coal is burnt completely in a bomb calorimeter in a current of oxygen. Sulphur in the coal is oxidised to sulphates. The ash from the bomb calorimeter is extracted with dilute hydrochloric acid. The acid extract is then treated with BaCl_2 solution to precipitate sulphate as BaSO_4 . The precipitate of BaSO_4 is filtered, washed, dried and heated to a constant weight.

From the weight of BaSO_4 formed, S is estimated as follows



Let the weight of coal sample = W g

Weight of BaSO₄ = x g

233 g of BaSO₄ = 32 g of S

$$x \text{ g of BaSO}_4 = \frac{32}{233} \times x$$

$$\% \text{ Sulfur} = \frac{32}{233} \times \frac{x}{W} \times 100$$

$$\text{Or } \% \text{ Sulfur} = \frac{32}{233} \times \frac{\text{Weight of BaSO}_4}{\text{Weight of coal taken}} \times 100$$

Significance

- Although sulphur increases the calorific value of fuel, yet its presence is undesirable because it gets oxidised to SO₂ and SO₃, which causes environmental pollution.
- Sulphur-containing coal is not suitable for preparing metallurgical coke. Presence of sulphur in coke used in the iron industry affects the quality and properties of steel.

4. **Ash** It is determined in the same way as in proximate analysis.

5. **Oxygen** It occurs both in organic and inorganic portions of coal and is determined indirectly by deducting the % of C, H, N, S and ash from 100

% of oxygen = 100 – % of (C + H + N + S + ash).

Significance

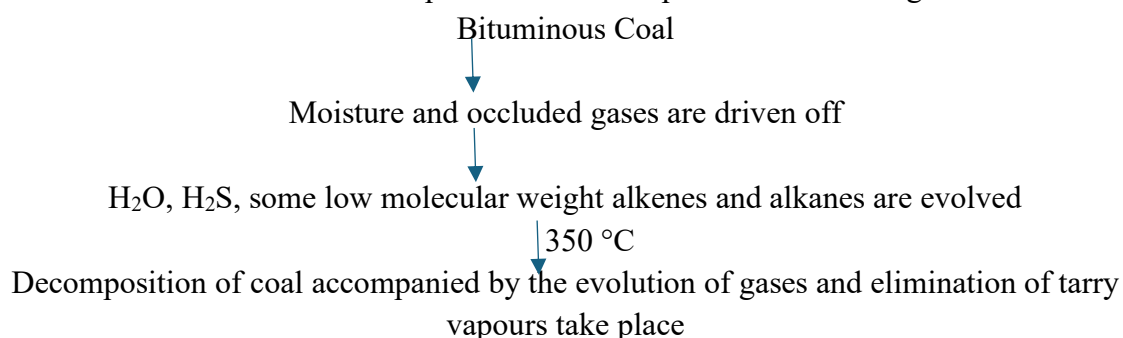
- Oxygen is present in coal in combined form. It is present in association with hydrogen; hence, it reduces the hydrogen available for combustion.
- Moreover, high oxygen-containing coals have high inherent moisture and hence low calorific values.
- Calorific value decreases about 1.7% for every 1% increase in oxygen. Thus, a good-quality coal should have low percentage of oxygen.

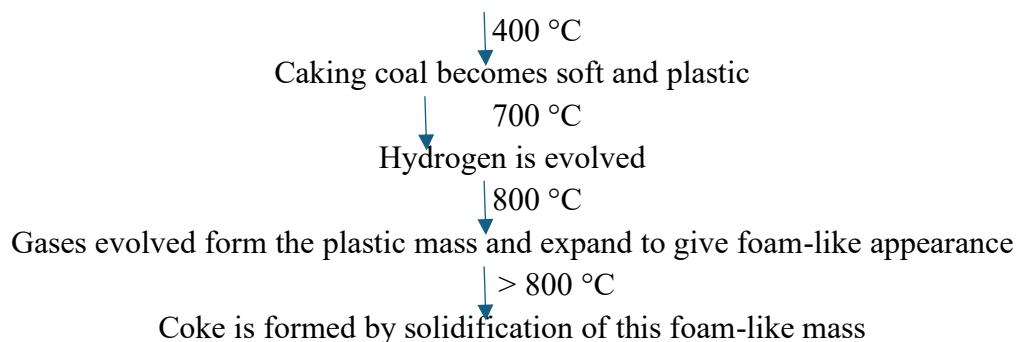
4. Carbonisation of Coal

When coal is heated to a high temperature in the absence of air, it loses volatile matter and gets converted into a white, dense, lustrous, strong, porous and coherent mass, which is richer in carbon content than the original fuel. This is known as *coke* and the process of converting coal into coke in the absence of air is known as carbonisation of coal.

4.1 Process of carbonisation

The process of carbonisation can be depicted with the help of the flow chart given below





4.2 Types of carbonisation

The properties of the coke produced depend on the type of coal used, temperature and the rate of carbonisation. Depending upon the temperature, carbonisation is of two types:

1. Low-temperature carbonisation
2. High-temperature carbonisation

(i) **Low temperature carbonisation** When destructive distillation of coal is carried out at 500–700 °C, it is called low temperature carbonisation. It is used mainly for the manufacture of domestic fuel. The yield of coke is about 75–80%. The coke thus produced contains 5–15% volatile matter and is not strong enough to be used as metallurgical fuel. It is highly reactive, easily ignited and is a valuable, smokeless domestic fuel. In low-temperature carbonisation, the amount of liquid products is relatively larger. The gas obtained as a by-product during low-temperature carbonisation has high calorific value of about 6500–9500 kcal/m³ and the yield is about 130–150 m³/ton of the coal carbonised. It is a valuable gaseous fuel. The tar obtained as a by-product contains more of paraffinic hydrocarbons and small amount of aromatic hydrocarbons along with phenols and various other nitrogenated compounds.

(ii) **High temperature carbonisation** It is carried out at 900 °C–1200 °C and is used for the production of pure, hard, strong and porous metallurgical coke containing 1–3% volatile matter. The yield of coke is 65–75%. The by-product gas and tar have greater amount of aromatic hydrocarbons. The yield of by-product gas is 370–480 m³/ton of coal carbonised but its calorific value is lower (5000–6000 kcal/m³) than that produced in LTC. The formation of lower amount of paraffins and higher amount of gas, indicates that cracking of paraffinic compounds present in coal takes place at high temperature, resulting in the formation of gases and greater aromatisation.

4.3 Otto Hofmann's oven or By-product oven or Chamber oven

Construction It consists of a number of narrow rectangular chambers made of silica bricks. Each chamber is 10–12 m long, 3–4 m high and 0.4–0.45 m wide. The chambers are tightly closed so that no air is admitted. At the top of each chamber, there are three holes for charging the coal. It is also provided with a gas take off (which carries out volatile matter) and discharging doors at the base for the removal of coke. These carbonisation chambers are erected side by side with interspaces for combustion of fuel gas. Thus, the ovens get heated from both sides. The ovens (chambers) form a sort of battery of 10–100 ovens. One single oven is capable of holding 16–24 tons of coal.

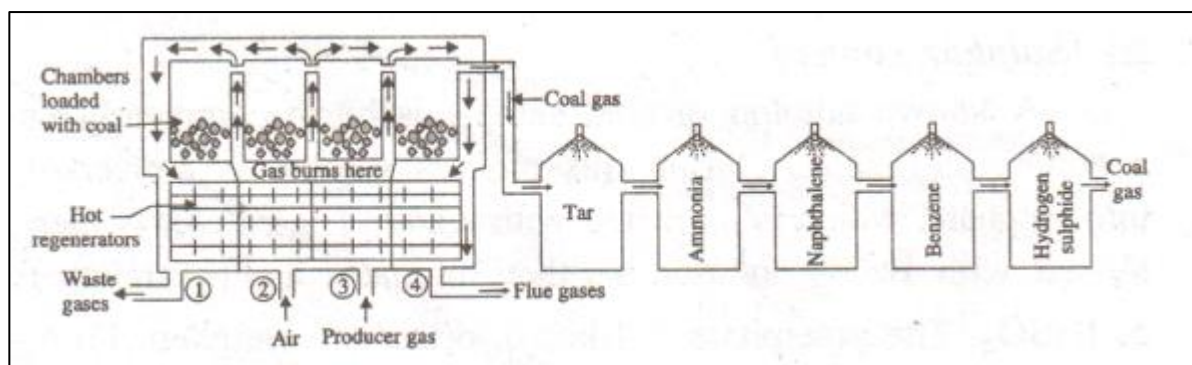


Fig. Otto Hofmann's coke oven method

Working

- Finely crushed coal is introduced through the charging holes at the top of the chambers which are
- then closed tightly at both ends to cut off the supply of air.
- The ovens are heated to 1200 °C by burning gaseous fuels (such as producer gas). Regenerative principle of heat economy is employed to achieve as economical heating as possible.
- The process of carbonisation starts in coal adjacent to the walls and moves towards the centre.
- As the coal is converted into coke, there is decrease in volume due to removal of volatile matter.
- Carbonisation of a charge of coal takes about 11–18 h.
- After the process is complete, red hot coke is pushed out by means of a ram, which is electrically driven. The coke falls into a quenching car.
- Quenching of red hot coke is carried out either by spraying water (wet quenching) or by passing inert gas such as N₂ from boilers (dry quenching).
- In wet quenching, sensible heat of coke is wasted, whereas in dry quenching the inert gases after quenching the coke become heated up and are circulated to the boilers where they generate steam. The coke produced by dry quenching is more strong, dense, graphitised and non-reactive. It is cheaper, dry and contains less dust than the wet quenched coke.

Recovery of by products

The gas coming out of the oven is known as 'coke oven gas' and is mainly composed of ammonia, H₂S, naphthalene, benzene, tar, moisture, etc. These are recovered as follows:

(i) Recovery of tar

The gases from the coke oven are passed through a tower in which liquor ammonia is sprayed. Tar and dust get collected in a tank below. The tank is provided with heating coils to recover NH₃. Ammonia is again sent to the top of the trickling tower and is used again.

(ii) Recovery of ammonia

The gases now enter another tower where water is sprayed. Ammonia goes into the solution as NH₄OH.

(iii) Recovery of naphthalene

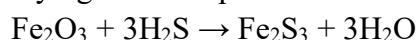
The gases then pass to a cooling tower where water at low temperature is sprayed. Naphthalene gets condensed which is then collected.

(iv) Recovery of benzene

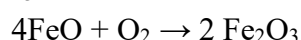
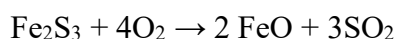
The gases then pass through a scrubber, where petroleum is sprinkled, resulting in the condensation of benzene and its homologues.

(v) Recovery of H₂S

The gases then enter a purifying chamber packed with moist Fe₂O₃. Here H₂S is retained.



After sometime, when all Fe₂O₃ is changed to Fe₂S₃, the purifier is exposed to atmospheric air, where Fe₂O₃ is regenerated.



(vi) Recovery of gas

The gas after passing through various condensers and scrubbers to remove the by-products mentioned above is finally collected in a gas holder. It is the coal gas whose calorific value is about 5000 kcal/m³.

5. Metallurgical coke

Coke is used as a heat source and reducing agent in metallurgy. Its properties depend on porosity, reactivity and the amount of volatile matter retained by coke during carbonisation. A good metallurgical coke should possess the following properties

(i) **Purity** The moisture, ash, sulphur and phosphorus contents should be very low. Moisture reduces calorific value whereas excess of ash hinders the heating and also helps in slag formation. The presence of sulphur and phosphorus gives undesirable products like SO₂, P₂O₃ and P₂O₅ on burning, which adversely affect the quality of the metal being produced. The presence of sulphur makes the coke brittle.

(ii) **Porosity** Coal should be porous so that oxygen can come in contact with carbon, which ensures efficient and complete combustion of the fuel in the furnace.

(iii) **Strength** Coke should be compact, hard and strong enough to withstand high pressure in the furnace as well as to withstand the abrasive action of the ores, flux, etc.

(iv) **Size** Metallurgical coke should be of medium size – neither too big nor too small. If the size is big, uniform heating is not possible, whereas small size of coke results in choking.

(v) **Combustibility** Coke should burn easily but at the same time it should not be very reactive.

(vi) **Calorific Value** The calorific value of coke should be high.

(vii) **Cost** It should be cheap and easily available.

(viii) **Calorific intensity** The calorific intensity of coke should be high enough to melt the metal.

6. Liquid Fuels

Liquid fuels are used extensively in industrial and domestic fields. Use of liquid fuels in internal combustion engines makes them very important fuels. The single largest source of liquid fuels is petroleum or crude oil (the term petroleum means rock oil. Latin-Petra means rock; oleum means oil) is a dark, greenish-brown viscous oil found deep inside the earth's crust. It is a mixture of

hydrocarbons such as straight chain paraffins, cycloparaffins or naphthalene, olefins and aromatics along with small amount of organic compounds containing oxygen, nitrogen and sulphur. Average composition of crude petroleum is:

Carbon	75.5–87.1%
Hydrogen	11.5–14.8%
Sulphur	0.1–3.5%
Nitrogen	0.4–0.9%
Oxygen	0.1–0.9%

6.1 Classification of petroleum

Petroleum is classified into three categories according to its composition:

1. **Paraffinic base petroleum** It is mainly composed of straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amounts of naphthenes and aromatic hydrocarbons.
2. **Naphthenic or asphaltic base petroleum** It contains mainly cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons.
3. **Mixed base petroleum** It contains both paraffins and asphaltic hydrocarbons.

6.2 Refining of Petroleum

Crude oil coming out from the oil well is a mixture of solid, liquid and gaseous hydrocarbons containing sand and water in suspension. After removal of dirt, water, sulphur and other impurities, this oil is subjected to fractional distillation. This process of removing unwanted impurities and separating petroleum into useful fractions with different boiling ranges is called refining of petroleum.

The process of refining involves the following steps:

1. **Separation of water (demulsification)** The crude oil from the well is an extremely stable emulsion of oil and salt water. The demulsification is achieved by *Cottrell's process*. The crude oil is allowed to flow between two highly charged electrodes where colloidal water droplets merge to form large drops which separate out from the oil.
2. **Removal of harmful impurities** NaCl and MgCl_2 corrode the refining equipments. These are removed by modern techniques like electrical desalting and dehydration. Harmful sulphur compounds are removed by treating the crude oil with copper oxide. Sulphur reacts with copper oxide forming copper sulphide, which is removed by filtration.
3. **Fractional distillation** Crude oil is heated to $400\text{ }^\circ\text{C}$ in an iron retort whereby all the volatile constituents, except asphalt or coke are evaporated. The vapours are then passed into a fractionating column, which is a tall cylindrical tower. The tower is hot towards the lower end and comparatively cooler at the upper end. It consists of a number of horizontal stainless-steel trays at short distances. These trays are provided with individual chimneys which are covered with a loose cap. As the vapours go up, fractional condensation occurs at different heights of the column. Higher boiling fractions condense first, while lower boiling fractions condense later as shown. The residue from the bottom of fractionating tower is vacuum-distilled to recover various fractions.

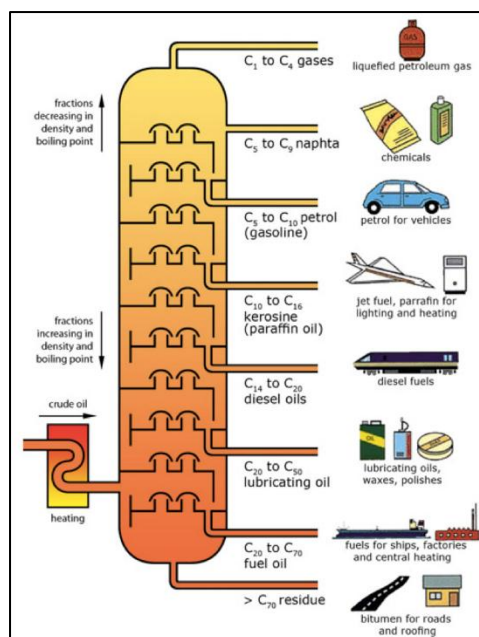
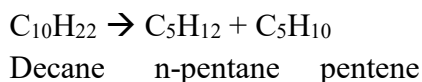


Fig. Fractional distillation of crude oil

6.3 Cracking

The crude oil obtained on fractionation yields approximately 20–30% gasoline, 30–35% middle oils and 20–25% heavy oils. Among all these fractions, gasoline (also called straight run petrol) is in maximum demand because of its use as fuel in the automobile industry. Hence, there is a need to convert the middle oil and heavy oil fractions into a more useful fraction gasoline. This is achieved by *cracking*. Cracking is defined as the process of converting high-molecular-weight bigger hydrocarbons into low-molecular-weight smaller hydrocarbons by the application of heat, with or without a catalyst.



Nearly 50% of today's gasoline is obtained by cracking. It is important to note that the characteristics of gasoline obtained by cracking are far more superior to the straight run gasoline. The methods of cracking are summarised below:

1. **Thermal cracking** When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking. The bigger hydrocarbons breakdown to give smaller molecules of paraffins, olefins and some hydrogen. This process may be carried out either in liquid phase or in vapour phase.

(a) **Liquid phase thermal cracking** By this method any type of oil (residue, fuel oil or gasoline) can be cracked. The charge is kept in liquid form by applying high pressure of the range of 100 kg/cm² at a suitable temperature of 475–530 °C. The cracked products are separated in a fractionating column. The octane rating of the product is 65–70.

(b) **Vapour phase thermal cracking** This method is suitable for oils which can be readily vaporised. The oil is first vaporised and then cracked at about 600–650 °C and under a low pressure of 10–20 kg/cm². It requires less time than the liquid phase method. Petrol obtained from vapour phase cracking has better antiknock properties, but poorer stability than the petrol obtained from liquid-phase cracking.

2. Catalytic cracking It is carried out in the presence of a catalyst at a much lower temperature and pressure. The catalyst used is usually a mixture of silica and alumina (hydrated aluminium silicate) or zeolites in the form of beads or pellets. There are two main types of catalytic cracking.

(a) Fixed bed catalytic cracking The vapours of the oil are preheated in a pre-heater to a temperature of 420–450 °C. It is then passed through a catalytic chamber containing either silica-alumina gel ($\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) or bauxite mixed with clay and zirconium oxide maintained at 425 °C–450 °C and 1.5 kg/cm² pressure. Cracking of heavy oil vapours takes place and 30–40% of the charge is converted into gasoline and about 3–4% carbon is formed which gets adsorbed on the catalyst bed. The cracked vapours then pass through a cooler where some gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a ‘stabiliser’ where the dissolved gases are removed and pure gasoline is obtained. After 8–10 h, the catalyst stops functioning because of the deposition of black layer of carbon formed during cracking. This is re-activated by burning off the deposited carbon. During the reactivation of the catalyst, the vapors of heavy oil are diverted through another standby catalytic chamber so that the reaction proceeds continuously.

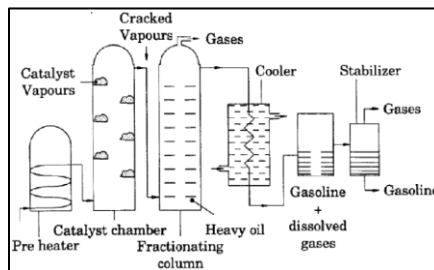


Fig. Fixed bed catalytic cracking

(b) Moving bed catalytic cracking This is also known as fluidised bed catalytic cracking. The feed oil is preheated. It is then mixed with powdered catalyst and the mixture of preheated heavy oil and powdered catalyst goes in a reactor maintained at 500 °C. Cracking of heavy oil takes place. Near the top of the reactor there is a centrifugal separator called cyclone) which allows the cracked vapours to pass on to the fractionating column but retains the catalyst powder. The catalyst powder gradually becomes heavier, due to coating with carbon formed and settles at the bottom. This is called *spent catalyst* and is forced by a blast of air to the regenerator maintained at 600 °C. In regenerator, carbon is burnt off and the catalyst is reactivated. The regenerated catalyst then flows through a standpipe to get mixed with fresh charge. The cyclone at the top of the regenerator allows the flue gases (e.g., CO_2) to escape retaining the catalyst particles.

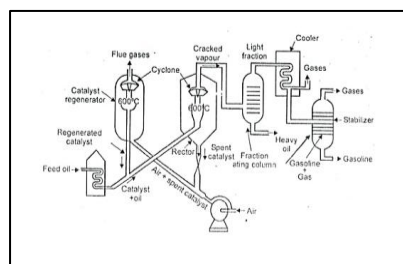


Fig. Moving bed catalytic cracking

6.4 Knocking

It is defined as the metallic sound similar to rattling of hammer produced in internal combustion engine due to immature ignition of fuel air mixture. An internal combustion engine uses either gasoline or diesel as fuel. A fuel combination (diesel or gasoline) is ignited in a cylinder in an internal combustion engine. The ignition is brought about by means of an electric spark (in petrol engines) or by compressing the air (in diesel engines). The gases evolved during ignition, force the piston down due to high pressure thus producing the power stroke. In a petrol engine the whole process comprises of four strokes;

(i) **Suction stroke** A mixture of air and gasoline fumes from the carburetor are drawn into the cylinder by the downward-moving piston..

(ii) **Compression stroke** The gas mixture is compressed as the piston rises. Compression ratio is the ratio of initial volume (volume at suction stroke) to final volume (volume at compression stroke). It is here that a low octane rating fuel might ignite and cause knocking.

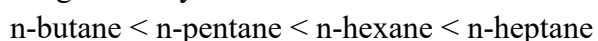
(iii) **Power stroke** Just before the piston reaches the top centre of the cylinder a spark from the spark plug ignites the gas mixture. The hot gases produced due to combustion increase the pressure and push the piston down.

(iv) **Exhaust stroke** This is the last stroke in which the piston rises up and expels the exhaust gases from the cylinder.

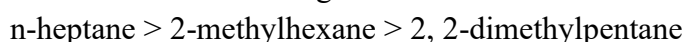
After that, the cycle is repeated. The fuel-air mixture should burn quickly and smoothly once a spark starts the reaction, allowing the expanding gas to easily push the piston down the cylinder. The efficiency of internal combustion engine depends on the compression ratio. Higher the compression ratio greater is the efficiency of the engine. To achieve maximum efficiency, a compression ratio of about 7–8 is required. Nevertheless, the fuel-air mixture may be heated above its ignition temperature if the compression ratio rises over a particular point, causing the fuel to spontaneously burn even before sparking. This is called pre-ignition. As a result of pre-ignition, the unburned fuel air mixture gets heated to such an extent that some of the hydrocarbons reach their ignition temperature and ignite all at once – explosively causing a metallic sound called knocking. Knocking decreases the efficiency of the engine and causes huge loss of energy and damage to piston and cylinder. Knocking depends on the chemical composition of the fuel, engine design, shape of head, location of plug, ports, etc., and also upon the running conditions.

6.4.1 Chemical structure and knocking

1. The knocking tendency decreases with increase in compactness of the molecule.
2. Knocking decreases with the increase in the number of double bonds and rings (cyclic structure).
3. With normal paraffins, the knocking increases with increase in length of the hydrocarbon chain. Thus, the knocking tendency increases from n-butane to n-heptane.



4. Knocking decreases as the branching in carbon chain increases.

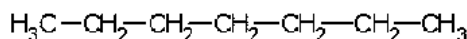


5. Aromatics such as benzene and toluene have very high antiknock properties. In general the tendency of fuel constituents to knock is in the following order :

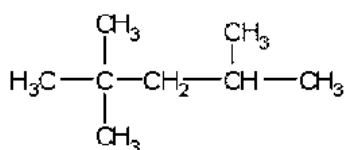
Straight chain paraffins > branched chain paraffins (i.e., isoparaffins) olefins > cycloparaffins (i.e., naphthalenes) > aromatics.

6.4.2 Octane Rating

In order to classify the fuels according to their knocking property, an arbitrary scale was provided by Edger in 1926, known as octane rating or octane number. Since n-heptane is known to knock extremely badly, its antiknock value was randomly set to zero. On the other hand, isooctane (2,2,4-trimethylpentane) has a high resistance to knocking and hence was arbitrarily assigned a value of 100.



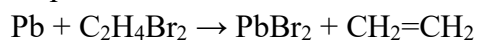
n-heptane
Octane number assumed to be zero



iso-octane (2,2,4-trimethylpentane)
Octane number assumed to be 100

Octane number of a fuel is defined as the percentage of isooctane in a mixture of isooctane and n-heptane, which has the same knocking characteristics as that of the fuel under examination, under same set of conditions. Thus, a fuel with octane number 80 is one which has the same combustion characteristics as a 80:20 mixture of isooctane and n-heptane.

6.4.3 Antiknocking agents By adding chemicals like alcohol and benzol, gasoline's octane number can be raised. This procedure is known as "blending.". The antiknock properties of gasoline are usually increased by adding tetraethyl lead (TEL). $\text{Pb}(\text{C}_2\text{H}_5)_4$ and the process is called 'doping'. Although TEL is a colorless liquid with a pleasant smell, it is extremely toxic. About 0.5 mL of TEL per liter is added for motor fuels and about 1 mL of TEL per liter is added for aviation fuel. Gasoline containing TEL is coloured with 2% red dye to indicate its poisonous nature. Knocking is considered a free radical mechanism. During combustion $\text{Pb}(\text{C}_2\text{H}_5)_4$ forms Pb and PbO . These act as free radical chain inhibitors and hence the propagation of the chain reaction leading to knocking does not take place. However, the environment is contaminated by lead and lead oxide vapors that are so produced. Lead oxide quickly transforms into metallic lead, which is then deposited on the piston head, cylinder walls, and spark plug. Hence, it is harmful to the engine. In order to solve these problems ethylene dibromide ($\text{C}_2\text{H}_4\text{Br}_2$) is also added, so that lead formed is converted into lead bromide, which is volatile and escapes into the atmosphere.

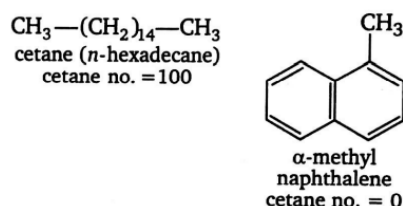


6.4.3 Unleaded petrol It is one where octane number is increased without the addition of lead compounds. High octane number compounds such as isopentane, isooctane, ethylbenzene, isopropyl benzene, methyl tertiary butyl ether (MTBE) are used. Out of these, MTBE is preferred because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing peroxy compound formation. Use of unleaded petrol requires the use of catalytic converter. A catalytic converter contains a catalyst (rhodium), which

converts the toxic gases (CO and NO) to harmless gases (CO₂ and N₂, respectively). Moreover, it oxidises unburnt hydrocarbon into CO₂ and H₂O.

7. Cetane Rating/Cetane Number

Cetane number is a measure of ignition quality of a diesel fuel. It is often mistaken as a measure of the fuel quality. It is actually a measure of the fuel's ignition delay. It is the measure of the ease with which the fuel will ignite under compression. The hydrocarbon cetane (n-hexadecane) has a very short ignition delay as compared to any diesel fuel and is assigned an arbitrary value of 100. α -methyl naphthalene has a long ignition delay compared to any other diesel fuel and hence is assigned a value of 0 (zero).



The percentage of cetane (n-hexadecane) in a mixture of cetane and α -methyl naphthalene that will have the same igniting properties as the fuel being tested under the same conditions is known as the cetane number of a diesel fuel.

For example, a diesel fuel will be assigned a cetane number of 60, if it has the same ignition characteristics as that of a mixture of 60% cetane (n-hexadecane) and 40% α -methyl naphthalene. The cetane value of a fuel depends upon the nature and composition of hydrocarbon. The straight chain hydrocarbons ignite quite readily, although aromatics do not ignite easily. Ignition quality order among the constituents of diesel engine fuels in order of decreasing cetane number is as follows:

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

Hydrocarbons are therefore excellent diesel fuels but bad gasoline fuels. A small amount of specific "preignition dopes," such as ethylnitrite, isoamyl nitrite, acetone peroxide, etc., can be added to diesel fuel to increase its cetane number.

High-speed and Low speed diesel In a high-speed diesel engine the time lag in getting the diesel droplets heated to ignition point is very small, about 1/500th of a second. Such diesel engines require diesel with cetane number in excess of 45 (up to 60). On the other hand, low speed diesel requires a cetane number of about 25. The cetane number of medium speed diesel is about 35.

8. Gaseous Fuels

Gaseous fuels can be obtained in many ways:

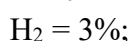
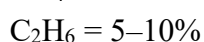
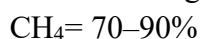
- From nature** - Natural gas and methane from coal mines.
- From solid fuels** - Producer gas, water gas, coal gas and blast furnace gas.
- From petroleum** - Refinery gases, LPG and gases from oil gasification.
- By fermentation of organic wastes** - Biogas.

8.1 Natural Gas

Natural gas is generally found to be associated with petroleum in nature and occurs near coal mines or oil fields. It is used not only as a fuel for domestic and industrial purposes but also as a raw material in various chemical syntheses.

- Natural gas that is derived from oil wells may be dry or wet. When natural gas is found to be associated with petroleum in oil well (it may be found dissolved in oil or may be present as a gas cap above the oil) it is called associated natural gas which is also termed as 'wet gas'.
- It is obtained from the oil-producing wells and is a mixture of methane and higher hydrocarbons such as n-propane, n-butane, isobutane, isopentane, etc.
- Wet natural gas contains less than 85% methane. Natural gas may also be present in reservoirs where there is no oil.
- This gas is called non associated natural gas or 'dry gas'. Dry gas is almost pure methane and once compressed it can be used directly as vehicle fuel.
- Dry or non-associated natural gas makes up around 60% of the world's natural gas supply. It should be mentioned that the phrases "wet" and "dry" solely describe the presence or absence of condensable hydrocarbons; they have nothing to do with water.

The approximate composition of natural gas is



remaining CO and CO₂. Apart from ethane natural gas also contains propane, butane, pentane, hexane, nitrogen and sometimes noble gases like helium are also present. Its calorific value varies from 12000 to 14000 kcal/m³. There are many uses for natural gas. It is used as fuel in automobiles, as well as in the home and business sectors. Acetic acid, butane, propane, ethane, and other substances are also prepared with it. It is a crucial component in the production of numerous fertilizers, antifreeze agents, polymers, medications, and textiles.

8.2 Compressed Natural Gas (CNG)

It is obtained by compressing natural gas to a high pressure of about 1000 atmospheres. These days, CNG is used as substitute for petrol and diesel. It is very economical and a clean fuel.

- It is better than LPG and is preferred over gasoline or LPG because it is safer than gasoline or diesel because its ignition temperature is higher than gasoline or diesel.
- It is lighter than air and disperses easily in air, minimising the risk of ignition. LPG being heavier than air settles at the ground level and hence is risky.
- As compared to gasoline, CNG produces lesser carbon monoxide on combustion.
- CNG-operated vehicles do not emit forbidden pollutants such as smoke, SO₂, SO₃, C₆H₆, HCHO, etc.

8.3 Liquefied Petroleum Gas (LPG)

Liquefied petroleum gas (LPG) is commonly used as a domestic fuel, industrial fuel and a fuel in motor vehicles. Chemically, it is a mixture of C₃ and C₄ hydrocarbons of the corresponding alkane and alkene series. It is generally obtained as a by-product during the cracking of heavy oils or from natural gas. The gas obtained by cracking is dehydrated, desulphurised and bottled in cylinders under high pressure. Highly odorous ethylmercaptan is added to it to detect leakage.

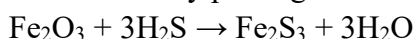
Composition LPG mainly contains paraffin hydrocarbons up to C₄ and its main constituents are n-butane, isobutane, butylene and propane with little or no propylene or ethane. These hydrocarbons exist in gaseous form under atmospheric pressure but can be liquified readily under pressure.

Properties

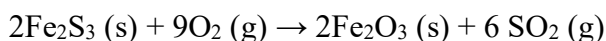
- It is a colourless, tasteless gas having very faint odour.
- It is 1.5–2.0 times heavier than air and can be easily liquefied at moderate pressure. The liquid is immediately transformed into vapour as soon as the pressure is released.
- It is non-toxic and non-poisonous but heavier than air. It pushes the air out of the room and can lead to suffocation.
- It is inflammable and has a high calorific value of nearly 27800 kcal/m³. This is nearly three times the calorific value of natural gas and seven times that of coal gas.

8.4 Coal Gas

It is obtained when coal is heated in the absence of air at about 1300 °C in gas retort or coke ovens. The fuel used for the purpose is a mixture of producer gas and air. Tar, NH₃, naphthalene and benzene are removed by passing the outgoing gases through water, cold water, petroleum and creosote oil, respectively. H₂S is removed by passing it over moist ferric oxide contained in a purifier.



When iron oxide is exhausted it is taken out from the purifier and exposed to air where it gets oxidised to ferric oxide.



The purified coal gas is finally stored over water in gas holders. Coal gas is a colorless gas having a characteristic odour. It is lighter than air and burns with a long smoky flame.

Its average composition is

H₂ = 40%; CH₄ = 32%; CO = 7%; C₂H₂ = 2%; C₂H₄ = 3%; N₂ = 4%; CO₂ = 1%.

Its calorific value is 4900 kcal/m³.

Uses

- As illuminant in cities and towns.
- As a fuel.
- As a raw material for ammonia production.
- In metallurgical operations for providing a reducing atmosphere.

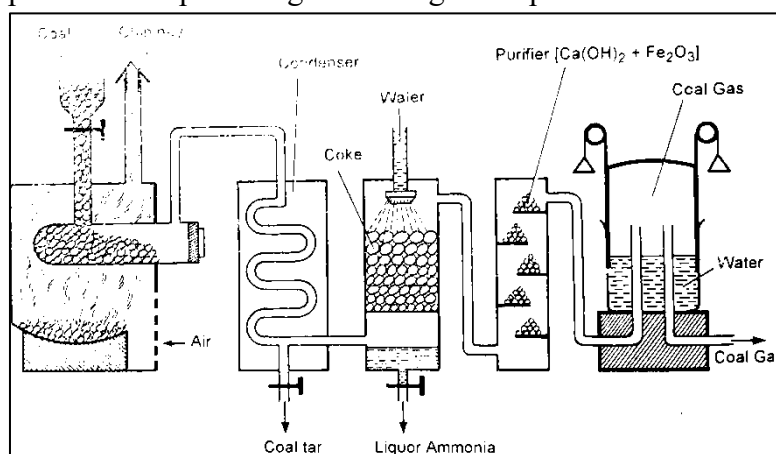


Fig. Manufacture of coal gas

8.5 Oil Gas

It is obtained by the cracking of kerosene oil.

Production

The plant used for the purpose consists of a strong cast iron retort enclosed in a coal-fired furnace. A bonnet is fitted at the mouth of the retort through a water seal. A pipe from the hydraulic main leads to the gas holder. This pipe has a testing tap from where the samples of gas can be taken for testing.

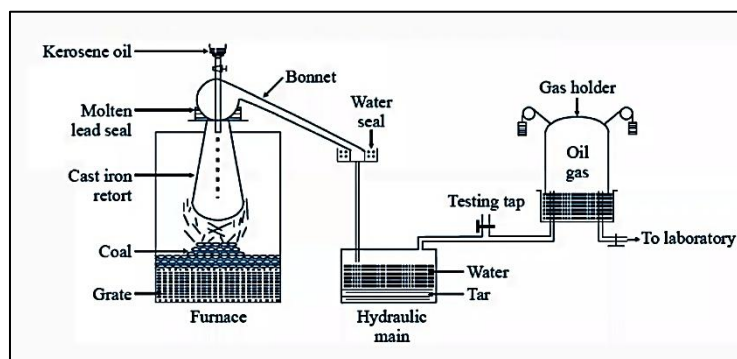


Fig. Manufacture of oil gas

Working

The retort is heated to red hot and a stream of oil is continuously allowed to fall on the red-hot bottom of the retort. The oil on coming in contact with the red-hot bottom immediately gets cracked into a number of lower gaseous hydrocarbons.



Kerosene oil Mixture of Hydrocarbons Tar

The gaseous mixture so obtained passes through the bonnet to a hydraulic tank (tank containing water) where tar gets condensed. Then at the testing tap, proper cracking of the gas is estimated from the color of the gas. A good oil gas should have a golden color. By properly adjusting the supply of air, golden color is obtained. The gas is finally stored over water in gas holders. The yield of gas is 40–50% and its calorific value is about 4500–5400 kcal/m³.

Approximate composition of oil gas

Methane (CH₄) = 25–30%

Hydrogen(H₂) = 50–55%

Carbon monoxide (CO) = 10–15%

Carbon dioxide (CO₂) = 3%

Applications

- It is used as laboratory gas.
- It is also used to improve the calorific value of water gas and the mixture of the two gases is called carbureted water gas.

8.6 Producer Gas

It is a mixture of carbon monoxide (combustible gas) and nitrogen (non-combustible gas).

Preparation It is prepared by passing air mixed with a little steam (about 0.35 kg/kg of coal) over red hot coal or coke bed maintained at 1100 °C in a special reactor called ‘gas producer’. Gas

producer is a steel vessel, about 3 m in diameter and 4 m in height. It is lined inside with refractory bricks to maintain a temperature of about 1100 °C. At the top of the reactor there is a cup and cone arrangement for feeding the charge and a side opening for the exit of producer gas. At the base there is inlet for air and steam and an exit for the ash form.

Reaction When a mixture of air and steam is passed over red-hot coke or coal bed at 1100 °C in gas producer the following reactions take place in different zones of the fuel bed.

(i) **Ash zone** It is the lowest zone consisting mainly ash. It is about 0.8 m thick. The function of this zone is

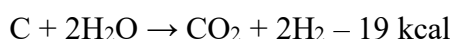
(a) To preheat the air and steam mixture as it passes through this zone.

(b) As ash is a bad conductor of heat it protects the grate (metal framework at the base for holding fuel) from intense heat of combustion.

(ii) **Combustion zone or oxidation zone** It is the zone next to the ash zone. In this zone carbon of the coal or coke burns in the presence of air to form CO and CO₂. The temperature of this zone is about 1100 °C.



(iii) **Reduction zone** Here carbon dioxide (produced in combustion zone) and steam combines with red hot coke to liberate free hydrogen and carbon monoxide:



As all the above reactions are endothermic the temperature of this zone falls to 1000 °C. For the production of producer gas only air can be used; however, the usage of steam along with air is beneficial because

(a) It raises the content of combustible component (CO + H₂), thereby increasing the calorific value.

(b) The endothermic reaction of steam and carbon prevents the temperature from rising too high and prevents the fusion of ash and refractory lining.

4. **Distillation zone** This is the uppermost part of the fuel bed. Here (400–800 °C), the outgoing gases give a portion of their heat to the down coming coal. This along with heat radiated from the reduction zone helps to distil the fuel, thereby volatile matter of coal is removed and comes out with outgoing gas.

Composition The average composition of producer gas is

Combustible gases

CO = 22–30%

H₂ = 8–12%

Non-Combustible gases

N₂ = 52–55%

CO₂ = 3%

It is insoluble in water and is poisonous in nature. Its calorific value is about 900–1300 kcal/m³

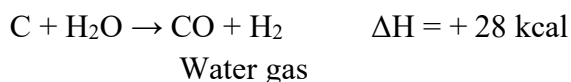
Applications

- As a reducing agent in metallurgical operations.
- As a fuel for heating open-hearth furnaces, muffle furnace and retorts (used in coke and coal

gas manufacture).

8.7 Water Gas

It burns with a blue flame and is often termed as 'blue gas'. It is a mixture of carbon monoxide and hydrogen with little amount of non-combustible gases such as carbon dioxide and nitrogen. Its calorific value is nearly 2800 kcal/m³ and is prepared by passing steam over red hot coke at about 1000 °C.

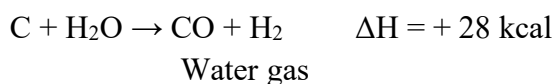


The above reaction being endothermic requires lot of heat to maintain the temperature of the furnace. If this heat is supplied from an external source the process would become uneconomical; hence, the reaction is carried out in two steps. In the first step air is blown to generate heat, and in the second step steam is blown and the formation of water gas takes place with the absorption of heat. These two steps are called blow and run periods, respectively.

Manufacture The gas generator is made up of steel with a refractory lining. It has a cup and cone arrangement at the top for feeding the coke. At the bottom it is provided with two separate inlets for steam and air supply. There is an outlet for the removal of ash at the bottom and for the exit of water gas near the top.

The following reactions are involved:

1. Air is passed through the coke bed when the carbon of the coke burns in the presence of the oxygen in air to produce carbon dioxide. This reaction is exothermic and the temperature of the fuel bed rises to 1000 °C. This is the *blow step* of the cyclic process.
2. When a sufficiently high temperature is attained the supply of air is cut off and then steam is blown through the red hot bed of coke. Steam combines with coke to form water gas.



The second step is the run step of the cyclic process. This step is endothermic and hence the temperature again begins to drop. Again the supply of steam is stopped and air is supplied. The cycle is repeated alternately to maintain the required temperature.

Composition

H₂ = 51%; CO = 41%; N₂ = 4%; CO₂ = 4%

Uses

Water gas is used as a fuel in furnace; it is used in Fischer–Tropsch process for the manufacture of synthetic petrol. Its mixture with hydrogen is used for the manufacture of methanol.

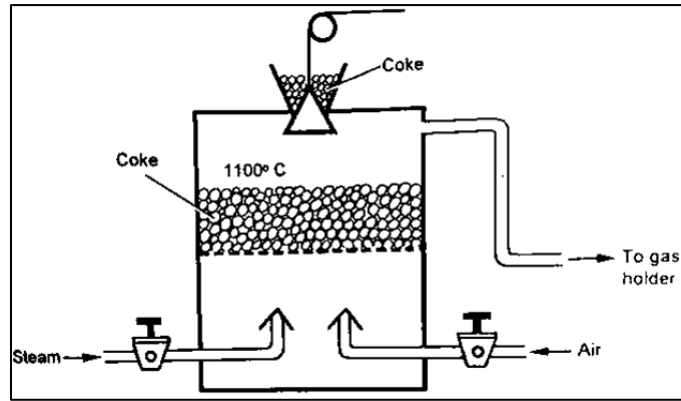


Fig. Manufacture of water gas

Carbureted water gas The calorific value of water gas is very low (2800 kcal/m^3). Its calorific value can be increased by mixing it with gaseous hydrocarbons obtained by the cracking of crude oils. This enhances the calorific value of water gas to 4500 kcal/m^3 . The average composition of carbureted water gas is

$\text{CO} = 23 - 28\%$

$\text{H}_2 = 34 - 38\%$

Saturated and unsaturated hydrocarbons = $30 - 48\%$

$\text{CO}_2 = 0.2 - 2.5\%$

$\text{N}_2 = 2.5 - 5\%$