18

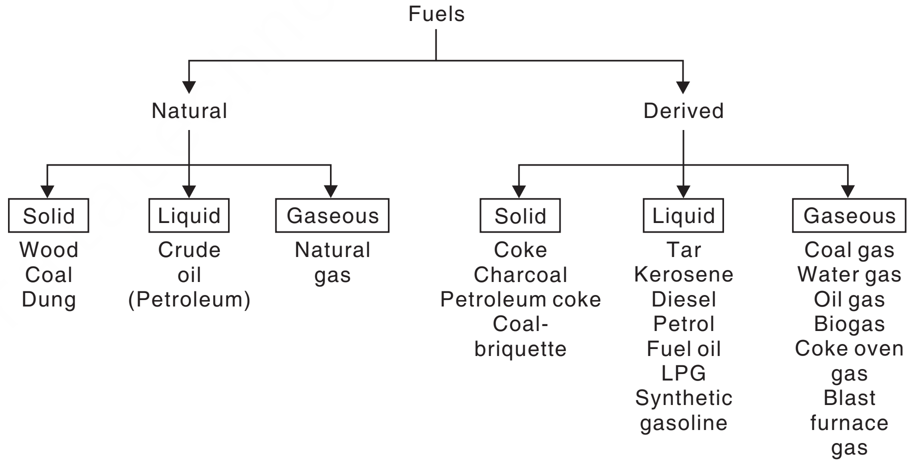
Fuels and Combustion

INTRODUCTION

Fuel is a combustible substance, which on combustion produces a large amount of heat, which can be used for various domestic and industrial purposes. The fuels commonly used contain carbon as the main constituent and some common fuels are wood, charcoal, kerosene, diesel, producer gas etc. *Fossil fuels* are non-renewable energy resources which were stored up millions of years ago by photosynthesis. The fossil fuels are coal, crude oil and natural gas.

The process of combustion involves oxidation of carbon, hydrogen etc. of the fuels to CO_2, H_2O, and the difference in the energy of reactants and the products are liberated as large amount of heat energy which is utilized.

Classification of fuels



CALORIFIC VALUE

There are different expressions for calorific values:

(*i*) The quantity of heat evolved by the combustion of unit quantity of fuel is its gross *calorific value* (GCV). Gross or higher calorific value is the quantity of heat liberated by combusting unit mass of fuel in oxygen, the original material and the final product of combustion being at a reference temperature of 25°C and the water obtained in the liquid state, represented by GCV or HCV.

(*ii*) *Net calorific value* (NCV) is the quantity of heat evolved when a unit quantity of fuel is burnt in oxygen, the original material and the final products of combustion being at a reference temperature of 25°C and the water obtained from the fuel being at the vapor state. The net calorific value is hence always less than the gross calorific value by the amount corresponding to the heat of condensation of water vapours *i.e.,* 587.0 kcal/kg.

$\therefore$ NCV = HCV – Latent heat of water vap. formed

= HCV – Mass of hydrogen × a × Latent heat of steam

since 1 part by mass of hydrogen produces 'a' part by mass of water.

Units of calorific value. The calorific value is expressed in either calorie/gm (cal/gm) or kilocalorie/kg (kcal/kg) or British thermal unit/lb (B.T.U/lb) in the case of a solid and a liquid fuel.

In the case of gaseous fuels, the units are kcal/m^3 or B.T.U./ft^3.

Determination of Calorific Value

Bomb calorimeter. The apparatus which is used to determine the calorific value of solid and liquid fuels is known as Bomb calorimeter (Fig. 18.1).

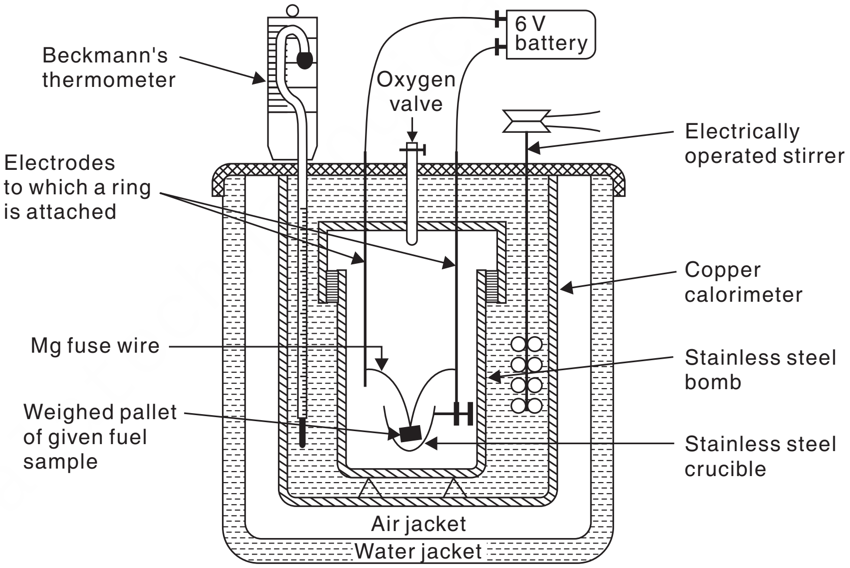


Fig 18.1 Bomb calorimeter.

The apparatus consists of a cylindrical stainless steel bomb, the lid of which is screwed to the body to make it air-tight. Through the lid there is one oxygen inlet valve and two electrodes. In the bomb there is nickel crucible attached to a ring. The sample of fuel is placed in the crucible. An electrically heated magnesium wire touches the sample. The bomb is placed in a copper calorimeter, which is surrounded by an air jacket and water jacket which minimises the heat loss due to radiation. There is a stirrer and a Beckmann's thermometer which can accurately measure the temperature upto $n/100^{th}$ of a degree.

A weighed mass of a fuel placed in the crucible is allowed to burn in oxygen by electric spark across the electrode and the heat liberated is measured by the principle of calorimetry *i.e.,* the heat liberated is taken by calorimeter and water. The initial and final temperatures of the calorimeter are noted.

Calculation: m = mass of fuel pellet (g)

W = mass of water in the calorimeter (g)

w = water equivalent of calorimeter (g)

t_1 = initial temperature of calorimeter.

t_2 = final temperature of calorimeter.

HCV = gross calorific value of fuel.

$$L = HCV = \frac{(W + w)\,(t_2 - t_1)}{m}\ \text{cal/gm.}$$

The water equivalent of calorimeter is determined by burning a fuel of known calorific value and using the above equation. The fuels used in the above purpose are benzoic acid (GCV = 6325 kcal/kg) and naphthalene (GCV = 9688 kcal/(kg). The correction factors used to get accurate results include:

(*i*) *Fuse wire correction*. Heat liberated during sparking should be subtracted from heat liberated.

(*ii*) *Acid correction.* Fuels containing Sulphur and Nitrogen if oxidised, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions).

(*iii*) *Cooling correction*. The rate of cooling of the calorimeter from maximum temperature to room temperature is noted. From this rate of cooling (*i.e., dt*°/min) and the actual time taken for cooling (*t* min) then correction (*dt* × *t*) is called cooling correction and is added to the $(t_2 - t_1)$ term.

$$\therefore \qquad L = \frac{(W + w)\,(t_2 - t_1 + \text{Cooling correction}) - (\text{Acid} + \text{fuse correction})}{m}.$$

The approximate calorific value of a fuel can be determined by knowing the amount of constituents present: Gross or higher calorific value (HCV) from elemental constituents of a fuel.

H = 34500 kcal/kg; C = 8080 kcal/kg; S = 2240 kcal/kg

Oxygen present in the fuel is assumed to be present as water (fixed hydrogen). Available H in combustion of the fuel is

$$= \text{Total hydrogen} - \text{Fixed hydrogen}$$

$$= \text{Total hydrogen} - \frac{1}{8}\ \text{mass of oxygen in fuel.}$$

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

$$HCV = \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{0}{8}\right) + 2240\ S\right] \text{kcal/kg}$$

where C, H, O, S are the percentages of carbon, hydrogen, oxygen and sulfur in the fuel. Oxygen is assumed to be present in combination with hydrogen as water,

$$\therefore \qquad LCV = \left[HCV - \frac{9}{100}\ H \times 587\right] \text{kcal/kg.}$$

$$= [HCV - 0.09\ H \times 587]\ \text{kcal/kg.}$$

($\because$ 1 part of H gives 9 parts of water and the latent heat of steam is 587 kcal/kg).

Example 1. *A coal has the following composition by weight C = 90%, O = 3%, S = 0.5%, N = 0.5% and ash = 2.5%. Net calorific value of the fuel was found to be 8490.5 kcal/kg. Calculate the percentage of H and GCV.*

Sol.

$$\begin{aligned}\text{HCV} &= \text{net calorific value} + (0.09\text{ H} + 587)\text{ kcal/kg}\\ &= (8490.5 + 0.09\text{ H} + 587)\text{ kcal/kg} \qquad [\because\ \text{H} = \%\text{ of hydrogen}]\\ &= (8490.5 + 52.8\text{ H})\text{ kcal/kg.}\end{aligned}$$

$$\begin{aligned}\text{HCV} &= \frac{1}{100}\left[8080 \times 90 + 34500\left(\text{H} - \frac{3}{8}\right) + 2240 \times 0.5\right]\text{ kcal/kg.}\\ &= 7754.8 + 345\text{ H} = \text{kcal/kg.}\\ &= 7754.8 + 345\text{ H} = 8490.5 + 52.8\text{ H.}\end{aligned}$$

$$\therefore \quad 7754.8 + 345\text{ H} = 8490.5 + 52.8\text{ H.}$$

or

$$292.2\text{ H} = 1335\%$$

$$\therefore \quad \text{H} = 4.575\%$$

$$\therefore \quad \text{HCV} = (8490.5 + 52.8 \times 4.575) = 8731.8\text{ kcal/kg.}$$

Example 2. *On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water was increased from 26.5°C to 29.2°C; water equivalent of calorimeter and latent heat of steam are 385 and 587 cal/g, respectively. If the fuel contains 0.7% H, calculate HCV and NCV.*

Sol.

$$\begin{aligned}\text{HCV} &= \frac{(\text{W} + w)\,(t_2 - t_1)}{m} = \frac{(385 + 3500)\,(29.2 - 26.3)}{0.83}\\ &= 12{,}638\text{ cal/g.}\\ \text{NCV} &= (\text{HCV} - 0.9\text{ H} \times \text{L})\text{ cal/g}\\ &= (12{,}638 - 0.9 \times 0.7 \times 587)\text{ cal/g}\\ &= 12{,}601\text{ cal/g.}\end{aligned}$$

Boy's Gas Calorimeter. It is used for measuring the calorific value of gaseous and liquid fuels (Fig. 18.2).

In the apparatus (Fig. 18.2) known volume of gas is burnt at a uniform rate by a burner. Around the burner there is a chimney containing coils wherein water at a constant rate is passed. Separate thermometers measure the incoming and outgoing water temperatures (t_1 and t_2) .

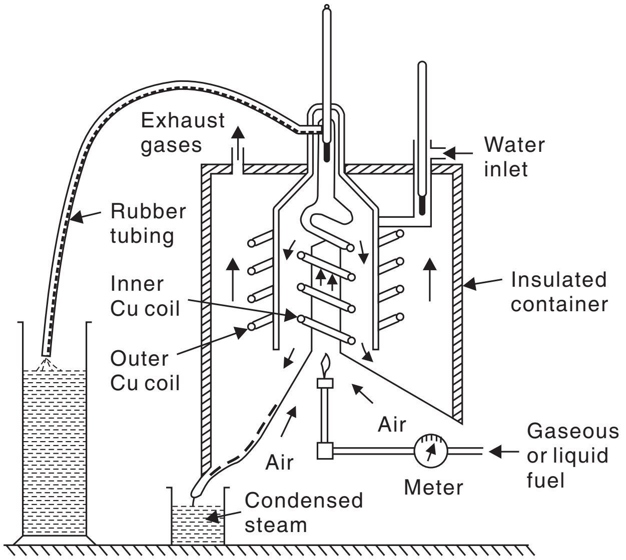


Fig. 18.2 Boy's gas calorimeter.

Let V = volume of gas burning.

W = mass of cooling water used in time t.

t_1 and t_2 = Incoming and outgoing water temperatures

m = mass of steam condensed in time t.

L = HCV.

We get $L = \dfrac{W(t_2 - t_1)}{V}$

Mass of H_2O condensed per m^3 of gas = m/v kg.

Latent heat of steam per m^3 of gas

$$= \frac{m \times 587}{V} \text{ kcal}$$

$$\therefore \qquad \text{NCV} = \left[L - \frac{m \times 587}{V}\right] \text{kcal/m}^3.$$

Example 3. *Calculate the volume of air required for complete combustion of 1 m^3 of a gaseous fuel having the composition: $CO = 46\%$, $CH_4 = 10\%$, $H_2 = 40\%$, $C_2H_2 = 2\%$, $N_2 = 1\%$ and the remaining being CO_2.*

Sol. Let the gaseous fuel be 1 m^3

$$CO + \frac{1}{2} O_2 = CO_2$$

Volume of O_2 required = $0.46 \times \dfrac{1}{2} = 0.23$ m^3

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Volume of O_2 required = $0.1 \times 2 = 0.2$ m^3

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

$$\text{Volume of } O_2 \text{ required} = 0.4 \times \frac{1}{2} = 0.2 \text{ m}^3$$

$$C_2H_2 + 2\frac{1}{2} O_2 = 2CO_2 + H_2O$$

$$\text{Volume of } O_2 \text{ required} = 0.2 \times \frac{5}{2} = 0.05$$

Total O_2 required = $(0.23 + 0.2 + 0.2 + 0.05)$ m^3 = 0.68 m^3

$\therefore$ Volume of air required = $0.68 \times \dfrac{100}{21}$ m^3 = 3.238 m^3.

SOLID FUELS

Wood

Wood is derived from trunks and branches of trees. It contains about 15% moisture after airdrying. Wood contains lignocellulose—wood pulp mainly consists of α cellulose and a very small amount of β cellulose, resins and proteins. The average composition of wood on moisture-free basis is C = 55%, H = 6%, O = 43% and ash = 1%. Wood is largely used as domestic fuel, its use as engineering fuel is restricted. Calorific value varies from 4000 to 6400 Btu/lb.

Coal

Coal is the most important solid fuel and derived from prehistoric plants. Coal is highly carbonaceous and composed of C, H, N, and O and non-combustible inorganic matter.

Origin. Vegetable matter is first transformed into peat, then to lignite then into bituminous coal and finally to anthracite. The transformation period extends over millions of years through a continuous process. The continuity can be proved graphically by plotting oxygen and C percentages of coal at different stages of formation.

Classification of coal. Various types of coal are ranked according to the degree of coalification from the parent material wood as follows:

$$\text{Wood} \longrightarrow \text{Peat} \longrightarrow \text{Lignite} \longrightarrow \text{Bituminous coal} \longrightarrow \text{Anthracite}$$

With the progressive transformation of wood, the moisture, H, O, N, S, volatile matter content decrease whereas carbon content, calorific value and hardness increase.

1. *Peat* is regarded as the first stage of coalification of coal. The composition and properties of peat widely vary from place to place, depending on nature of the original plant material. It is extracted by hand cutting. It is an uneconomical fuel since it contains about 80–90% moisture. It is used as domestic fuel, in steam boilers, power stations and gas producers. Peat is also used as a fertiliser. Low temperature carbonisation of peat is used for getting peat coke and byproducts. Peat is easy to ignite and burns freely to give a long pleasant flame .

2. *Lignite* or brown coals are soft, brown coloured coal. Lignite is compact in texture, containing 20–60% moisture. Airdried lignite contains C = 60–70%, O = 20%. Its calorific value is 6500–7000 kcal/kg. It burns with a smoky flame. It is powdered, dried and pressed into briquettes and used for domestic purpose, for boilers and for production of producer gas.

3. *Bituminous coals* are black and usually banded with alternate very bright and dull layers. On the basis of carbon content bituminous is classified as:

(*a*) *Sub-bituminous coals.* (C content 70–78%, H 4–5% and O 20%). The airdried material has moisture content of 10–20%. Calorific value is 6800–7600 kcal/kg. It ignites easily and if low in S content, used for gaseous fuel production.

(*b*) *Bituminous coal* (C content 78–90%, calorific value is from 8000 to 8500 kcal/kg). Its chief use is for combustion in household, industrial furnaces and boilers, railway locomotives and thermal power stations. By carbonisation and gasification it is converted to coke, gaseous fuels like producer gas, water gas, coal gas, liquid fuels like coal tar fuels.

(*c*) *Semi-anthracite* is intermediate between bituminous coals and anthracite. It ignites more easily than anthracite. When air-dried moisture content is 1–2%, volatile matter = 10–15%. Calorific value is 8500–8800 kcal/kg.

4. *Anthracite* is the highest rank coal having highest percentage of C (92–98%), lowest volatile matter and moisture. Calorific value is 8400–8600 kcal/kg. It burns without smoke but ignites with difficulty, possesses no coking power. Its chief uses are in boilers, domestic ovens and metallurgical furnaces.

Occurrences. Peat deposits are found in Nilgiri hills, lignites occur in Assam, Kashmir, Rajasthan and Tamil Nadu. Bituminous coals are found in Bihar, Bengal, Madhya Pradesh,Chhattisgarh and Orissa. Anthracites are found in Kashmir and eastern Himalayas.

Analysis of Coal

Ranking of coal is done on:

(*a*) *Proximate analysis:* It consists of determination of percentages of (*i*) volatile carbonaceous matter, (*ii*) fixed carbon, (*iii*) ash and (*iv*) moisture of the airdried coal.

(*b*) *Ultimate analysis:* Consisting of determination of percentages of C, H, O, N and S.

(*c*) *Calorific value:* The coking properties are of importance for bituminous coals only. Other chemical and physical properties are specific gravity, surface area and porosity, refractive index etc.

(a) ***Proximate Analysis:***

(*i*) *Moisture:* 1 g of finely powdered airdried sample taken in a crucible and heated in an electrically heated hot air oven at 105°C–110°C for 1 hr. and again weighed after desiccation till constant weight.

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

(*ii*) *Volatile matter:* The dried sample left in the crucible along with the lid is heated in a muffle furnace at a 250°C ± 20°C for 7 minutes and then cooled, weighed after desiccation till constant weight.

$$\text{Volatile matter percentage (V.M.)} = \frac{\text{Loss in weight}}{\text{Wt. of coal sample taken}} \times 100.$$

(*iii*) *Ash:* The residual sample after the two above experiments in the crucible is heated in the furnace at 700°C ± 50°C for 1 or 2 hours without the lid. Then it is cooled, left in the desiccator and weighed till constant weight.

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

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

Significance: By taking away the latent heat of evaporation *moisture content* lowers the calorific value of coal. Hence, lower the moisture content, better the quality of coal. Similar is the effect of *volatile matter content,* which escapes unburnt so volatile matter content lowers with better quality of coal. Low volatile matter also reduces coking property of coal. *Ash* being non-combustible, reduces the calorific value of coal. Ash deposition also causes problems in the furnace walls and the ultimate disposal of ash is also a problem.

Higher the percentage of *fixed carbon,* higher is the calorific value and better is the quality of coal.

(b) ***Ultimate Analysis:***

(*i*) *Carbon and hydrogen:* Accurately weigh 1–2 gm of the coal sample and burn in a current of O_2 in combustion apparatus whereby CO_2 and H_2O are formed. CO_2 and H_2O are absorbed by previously weighed tubes containing KOH and anhydrous $CaCl_2$. The increase in weight gives the C and H content as follows:

$$\underset{12}{C} + O_2 \longrightarrow \underset{44}{CO_2} \quad \text{and} \quad \underset{112\text{ g}}{2KOH} + CO_2 \longrightarrow \underset{138\text{ g}}{K_2CO_3} + H_2O.$$

$$\underset{2}{H_2} + \frac{1}{2}O_2 \longrightarrow \underset{18}{H_2O} \quad \text{and} \quad \underset{111\text{ g}}{CaCl_2} + 7H_2O \longrightarrow \underset{237\text{ g}}{CaCl_2.7H_2O}.$$

$$\therefore \quad \text{Percentage of C} = \frac{\text{Increase in wt. KOH} \times 12 \times 100}{\text{Wt. of coal sample} \times 44}.$$

$$\text{and percentage of H} = \frac{\text{Increase in wt. } CaCl_2 \times 2 \times 100}{\text{Wt. of coal sample} \times 18}.$$

(*ii*) *Nitrogen:* About 1 g of accurately weighed coal sample taken in a Kjeldahl's flask along with conc. H_2SO_4, K_2SO_4 and heated. Then it is treated with excess of KOH and the liberated NH_3 is absorbed in known excess of standard acid solution. The excess acid is back-titrated with standard NaOH solution. From the volume of acid consumed N content is calculated as follows:

$$\text{Percentage of N} = \frac{\text{Volume of acid consumed} \times \text{Normality} \times 1.4}{\text{Wt. of coal taken}}.$$

(*iii*) *Sulfur:* While determining the calorific value of a coal sample in a bomb calorimeter, the S in the coal is converted to sulfate. Finally the washings containing sulfate is treated with dil. HCl and $BaCl_2$ solution, which precipitates $BaSO_4$ which is filtered in a sintered glass crucible, washed with water and heated to a constant weight.

$$\text{Percentage of S} = \frac{\text{Wt. of } BaSO_4 \times 32 \times 100}{\text{Wt. of coal sample in bomb} \times 233}.$$

(*iv*) *Ash content:* Ash content is determined similar to proximate analysis.

(*v*) *Oxygen content* = 100 – % of (C + H + S + N + ash)

Significance: Higher percentage of C and H increases the calorific value of coal and hence better is the coal. Higher the percentage of O, lower is the calorific value and lower is the coking power. Also, O when combined with H in the coal, H available for combustion becomes unavailable. S, although contributes to calorific value, is undesirable due to its polluting properties as it forms SO_2 on combustion.

Coke

Carbonisation or coking bituminous coal leads to the formation of coke. Coke obtained from coal with high volatile matter forms swelling coke which is soft coke, and from a mixture of high and low volatile coking bituminous coal (non-swelling) in coke ovens hard coke is obtained. Both soft and hard cokes are obtained by *high temperature carbonisation*. A smokeless fuel or semicoke is obtained from *low temperature carbonisation*.

Coke and Coal

- Coke possesses much strength and porosity compared to coal.
- By coking the undesirable sulfur content of coal is removed from coke and due to lower volatile matter content of coke it burns with a short flame. All these properties of coke make it suitable for metallurgical processes compared to coal.

Carbonisation of Coal

Depending on the operation temperature there are mainly two types of carbonisation processes, namely,

(*i*) Low temperature carbonisation (LTC) and (*ii*) High temperature carbonisation (HTC). Coarsely powdered coal taken in a closed retort and heated out of contact with air leads to the breakdown of coal with the formation of water, ammonia, other volatile matters, gases and coke. This process is called the *carbonisation of coal* or *coking of coal.*

Table 18.1: By-products of carbonisation of coal

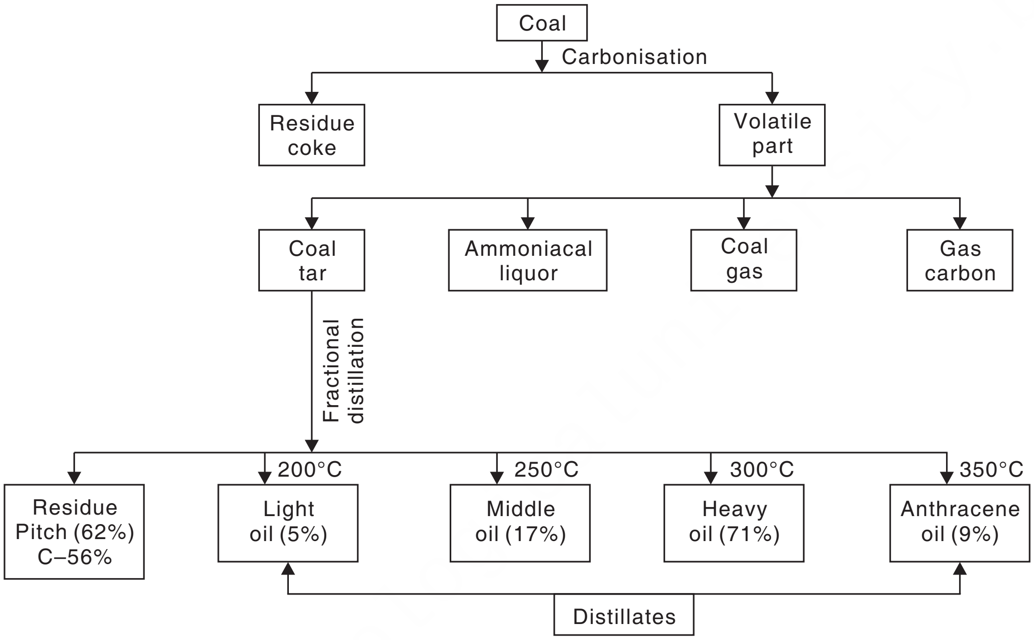


Table 18.2: Products (by fractional distillation)

Light oil	Benzene, Toluene, Xylene, Cumene etc.
Middle oil	Naphthalene, Phenol, Cresol, Pyridine etc.
Heavy oil	Cresol, Xylene, Naphthalene etc.
Anthracene oil	Phenanthrene, Anthracene, Quinoline etc.

(*i*) *Low temperature carbonisation (LTC).* In this process, coal is heated in steel retorts at 500°C–700°C. The yield of coke is 75–80% and it contains 8–12% volatile matter. The coke obtained is not mechanically strong but highly reactive and can be easily ignited to give smokeless flame and used as a domestic fuel. Low temperature carbonisation yields a very complex mixture of higher phenols, substituted aromatic hydrocarbons and other N and O containing compounds. Disinfectants are made from this tar. The coal gas obtained has calorific value of 6500 kcal/m^3 and is richer in hydrocarbons and poorer in hydrogen compared to the gas produced by HTC. The crude spirit corresponds to crude benzol of HTC but contains greater amount of paraffins, naphthalene and olefin.

(*ii*) *High temperature carbonisation (HTC).* It is carried out at 900°C–1200°C producing coke of good porosity, hardness, purity and strength and can be used in metallurgy. As all the volatile matters are driven off, the yield of coke is 65–75% containing 1–3% volatile matter. The retorts used are made of brick. The gas and tar yields are lower. The calorific value is lower, about 4500 kcal/m^3.

Distinction between high temperature carbonisation (H.T.C.) and low temperature carbonisation (L.T.C.) at a glance:

- Temperature ⇒ L.T.C. = 400–600°C
  H.T.C. = 1000–1400°C
- Economy ⇒ In L.T.C. less costly steel retorts are used whereas in the case of H.T.C. retorts made of fire bricks are used. The expenditure due to fuel is also less in the case of L.T.C. than that of H.T.C. as the working temperature is less.
- Nature of tar ⇒ The liquid volatile products are larger in quantity in the case of L.T.C., on the other hand the quantity of gaseous products is greater in the case of H.T.C. The formation of lower amount of paraffin and alicycilc compounds and higher amounts of aromatic compounds in the case of H.T.C. indicates that the process of aromatisation is greater in the case of H.T.C.
- Nature of other products ⇒ The amount of ammonia formed greatly increases with the rise of temperature showing that nitrogenous complexes are broken at higher temperature. The Tables 18.1 and 18.2 show the amount and nature of various products.
- Physical characteristics of tar ⇒ H.T.C. tars are darker in colour and more viscous than that of L.T.C. tars.
- Yield of tar ⇒ The yield of L.T.C. tar per ton of coal is much greater than that of H.T.C. tar.

There are two main types of oven for the manufacturing of coke:

(*a*) **Beehive oven:** It is a batch process and now obsolete. The firebrick chambers are of 2 m height and 3.5 m diameter and form the shape of a beehive. There are two openings, one at the top for charging the coals and the other on one side for the entry of air and also for removal of coke. Coal forms a layer of 60–90 cm depth. Carbonisation proceeds from the top to bottom and completes in 2–3 days. Heat is supplied by the burning of the volatile matter and hence no byproducts are recovered. The hot exhaust gases are utilised to run waste heat boilers to increase the heat efficiency. At the end of carbonisation, the coke is quenched by water and raked out through the side door, leaving the oven hot enough to start the next batch. The yield of coke is 80% of the coal charged (Fig. 18.3).

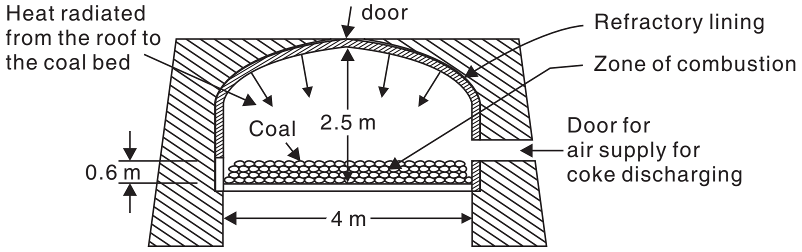


Fig. 18.3 Beehive coke oven.

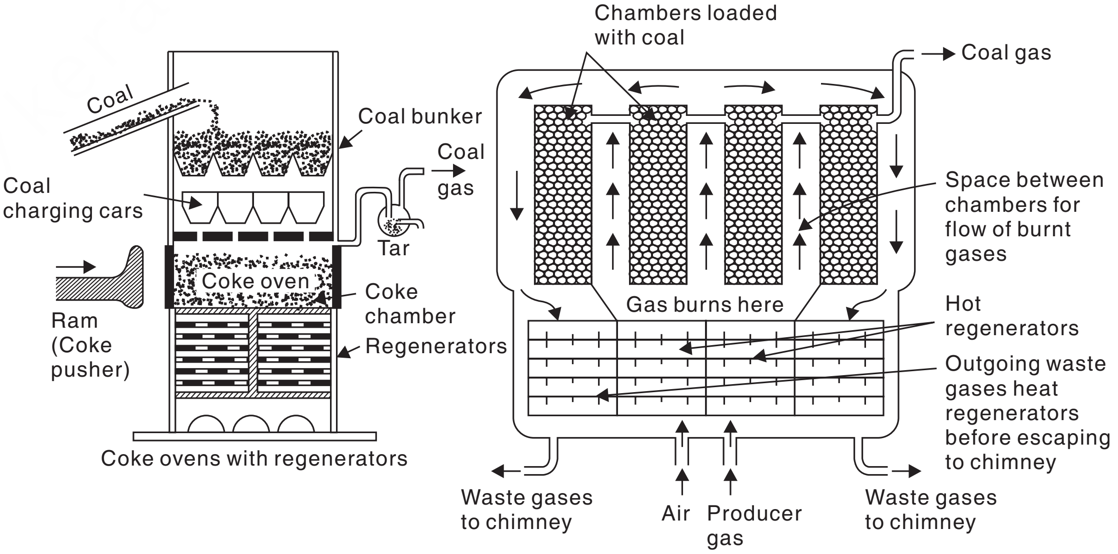
The limitations of the process are (*i*) no recovery of byproducts, (*ii*) coke yield is low, (*iii*) the exhaust gases cause pollution, (*iv*) process is not flexible.

(*b*) **Byproduct coke oven:** In this process coal is heated in combustion chambers, separate from carbonisation chambers. The thermal efficiency has been increased and the valuable byproducts are recovered. The coke ovens are made of silica bricks and the temperature is about 1350°C to 1450°C. The batch process is made continuous by building ovens in a battery. The oven consists of number of narrow silica chambers (10 m × 3 m × 0.4 m) erected side by side with vertical flues in between them. There is a charging hole at the top, a gas off take and a refractory lined cast iron door at each end. It is heated externally by a portion of coal gas produced by the process itself or by producer gas or by blast furnace gas.

Highlights:

- There are two main types of coking of coal:
  (*i*) Beehive and the (*ii*) by product coking.
- Beehive coking is obsolete. It is a batch process causing a large amount of pollution. A portion of coal is burnt inside the retort to generate heat for coking.
- In byproduct coking, air is excluded so that no burning takes place within the oven, heat is supplied from the hot flue gases and 40% of the oven gas (coal gas) generated is burnt to heat the battery of ovens and the rest is used for domestic fuel locally.

Finely crushed coal is charged through the hole at the top and in a closed system it is heated to 1200°C. The flue gases produced during combustion pass their sensible heat to the checker brick-work, which is raised to 1000°C. The flow of heating gases is then reversed and the hot checker bricks heat the inlet gas. This cycle continues till the volatile matter lasts. Carbonization takes about 11 to 18 hours, after which the doors are opened and the glowing coke mass is discharged by machine driven coke-pusher into coke-quencher. The hot coke is quickly quenched by water spraying. 'Dry quenching' is also done by circulating flue gases over hot coke and the hot gases are utilised to run waste heat boilers (Fig. 18.4).



Coke ovens with regenerators

Fig. 18.4 Otto Hoffman's byproduct coke oven with regenerators.

Recovery of byproducts: The gases coming out at 600°C–700°C get a spray of flushing liquor at the goose-neck of the standpipe and the temperature is reduced to 80°C. Tar and steam get condensed. The 'Coke oven gas' is composed of NH_3, H_2O; tar contains naphthalene, benzene, moisture etc.

(*i*) Coal tar is condensed in the tank below.

(*ii*) Ammonia is recovered partly as aqueous solution and partly as sulfate.

(*iii*) Naphthalene is recovered by passing the gas through a tower where water is sprayed at very low temperature which condenses the naphthalene.

(*iv*) Benzene is recovered similarly by spraying petroleum.

(*v*) H_2S is recovered by passing the gas through moist Fe_2O_3 as:

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

Fe_2S_3 is again regenerated by exposing to atmosphere

$$Fe_2S_3 + 4O_2 \longrightarrow 2FeO + 3SO_2$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

Beehive ovens are located in Jharia, Raniganj, Bokaro-Ramgarh in large numbers in India whereas byproduct coke ovens are on large numbers in Giridih, Durgapur, Jamshedpur, Bhilai, Rourkela, Bokaro etc.

LIQUID FUELS

Petroleum or crude oil is a deep brown oil consisting of mainly hydrocarbons, paraffins, naphthenes and aromatics in varying proportions. Sulfur, nitrogen and oxygen are present in the form of derivatives of hydrocarbons in the oil. The average ultimate analysis shows C ⇒ 83–87%, H ⇒ 11–14%, S ⇒ 0.5–3%, N ⇒ 0.1% and O ⇒ 2–3%. Practically all metals are found in petroleum, the most common are Si, Fe, Al, Ca, Mg, Ni.

Occurrence: The crude oil has been derived from the organic matter originally present in marine sediments. The dead organic matter settles down to the bottom of shallow seas and lagoons. The settled debris is attacked by anaerobic bacteria, whereby most of the organic compounds are destroyed and the remaining unsaturated fatty oils and fatty acids undergo polymerization.

Classification of petroleum. There are three main types petroleum according to chemical nature:

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

(*b*) Asphalt-base crude contains mainly naphthenes and cycloparaffins with smaller amounts of paraffins and aromatics.

(*c*) Mixed base crude contains both the above type of compounds but rich in waxes. About 90% crude produced at present fall in this last category.

Petroleum

Drilling: Oil is brought to the surface by drilling holes upto the oil bearing surface. By the hydrostatic pressure of natural gas the oil is pushed up or it is pumped up by means of a pump. Two coaxial pipes are lowered to the oil reservoir, through the outer pipe compressed air is forced, whereby the oil is forced out through the inner pipe. This crude oil is sent to the refineries for further processing and refining of the crude oils (Fig. 18.5).

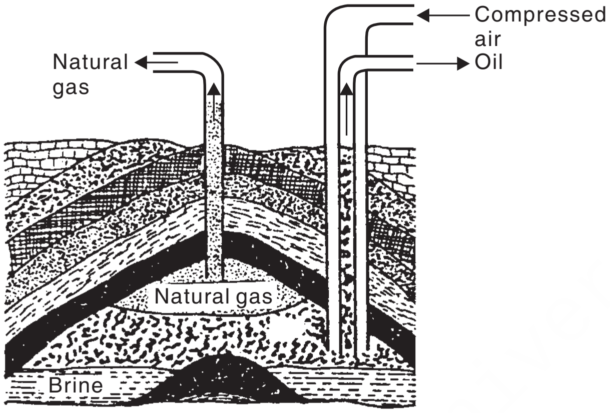


Fig. 18.5 Mining of crude oil and use of air-lift pump.

Refining: After removal of dirt, water and natural gas, the crude oil is separated into fractions by distillation and the fractions obtained are subjected to simple purification procedures or complex treatments to yield different petroleum products. All these steps are under petroleum refining which include:

1. **Coltrell's process.** Crude oil is intimately mixed with water forming an emulsion. The water is separated from the oil by passing the emulsion through Coltrell's electrostatic precipitator.

2. **Removal of objectionable compounds.** Sulfur compounds have objectionable properties of pollution so they are removed prior to distillation as copper sulfide by treatment with copper oxide.

3. **Petroleum distillation.** The crude oil is subjected to distillation to about 400°C temperature in an iron retort whereby all volatile components except the solid residue are distilled out. These are separated in a fractionating column consisting of a tall tower where the higher boiling fractions condense first. This distillation is a continuous process and the following fractions are obtained (Fig. 18.6) (Table 18.3).

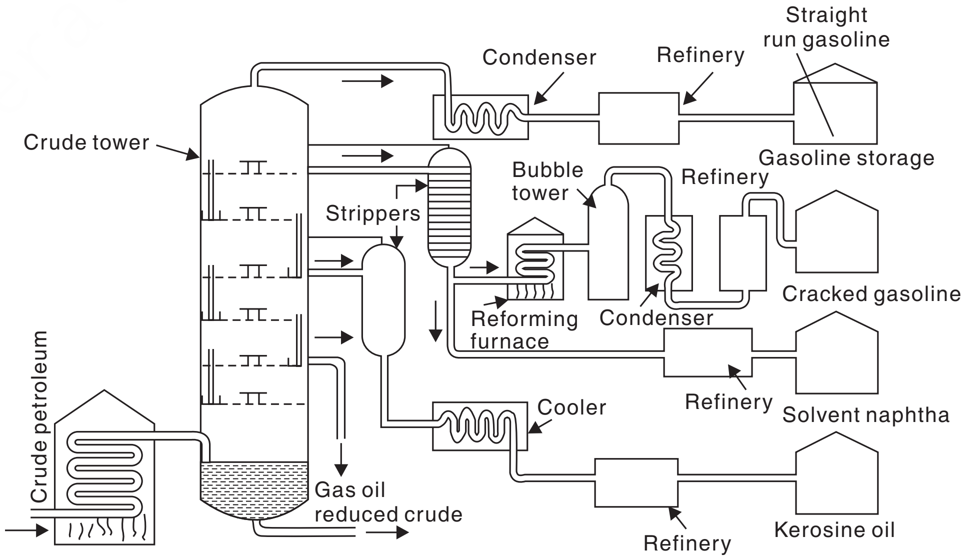


Fig. 18.6 Petroleum distillation.

(*a*) **Gasoline** is obtained upto 200°C. The naphtha is condensed and subjected to refining for the removal of sulfur, diolefins after refractionating.

(*i*) Petroleum ether boiling between 40°C–70°C and
(*ii*) Benzene boiling between 70°C–90°C and
(*iii*) Gasoline boiling between 90°C–200°C all are obtained.

Its calorific value is 14,250 kcal/kg and is used as a fuel for internal combustion engines in automobiles and aircrafts.

(*b*) **Solvent naphtha** is obtained as a side steam between 200°C–250°C. This contains some gasoline, which is passed back to the main fractionating column. Naphtha contains 6-10 carbon atoms.

(*c*) **Kerosene oil** is obtained between 250°C–300°C. The lower boiling fraction mixed with it is returned to the main column. Bottom liquid is refined and finally can be used as domestic fuel having calorific value of 1100 kcal/kg.

(*d*) **Gas oil** is obtained between 300°C–350°C. This is passed through a cooler and then extracted with liquid SO_2 to remove sulfur. It is used as a diesel engine fuel with calorific value of 11000 kcal/kg.

(*e*) The *residual liquid* coming out from the bottom on subsequent treatment yields lubricating oil, vaseline, grease, paraffin wax, asphalt-bitumen, petroleum, coke etc.

Table 18.3: Common fractions from crude

Fraction	*Boiling range*	*Composition*	*Uses*
Uncondensed gas	Within 30°C	C_1 to C_4	As domestic or industrial fuel under the name LPG (Liquefied petroleum gas)
Petroleum ether	30°C–70°C	C_5–C_7	As a solvent.
Gasoline or petrol	90°C–200°C	C_5–C_9	As a motor fuel solvent and dry washing
Naphtha	200°C–250°C	C_9–C_{10}	As a solvent
Kerosene oil	250°C–300°C	C_{10}–C_{16}	As fuel for domestic and industrial uses
Diesel oil	300°C–350°C	C_{10}–C_{18}	As a fuel for diesel engine
Heavy oil	320°C–400°C	C_{17}–C_{30}	For different fractions

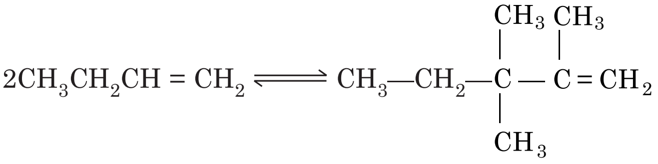
Cracking Process

Cracking is the process in an oil refinery by which heavier fraction from the fractional distillation converted into useful lighter fractions by the application of heat, with or without catalyst, *i.e.,* cracking is a process by which larger molecules break up into smaller ones. The chief application of commercial cracking in all the refineries is for the production of gasoline from gas oils. Other uses include the production of olefins from naphthas and gas oils. The surplus of heavier petroleum fractions are also cracked to get petrol. There are two methods of cracking.

1. *Thermal Cracking:* When cracking is carried out without any catalyst at high temperature from 450°C–750°C at pressures ranging from 1–70 atms, it is called *thermal cracking*. The important reactions are decomposition, dehydrogenation, isomerization and polymerization. The paraffins decompose to lower mol. wt. compounds, like paraffin and an olefin.

$$\underset{n\text{-decane}}{CH_3(CH_2)_8CH_2} \longrightarrow \underset{n\text{-hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{butene-1}}{CH_3CH_2CH = CH_2}$$

The olefins formed isomerizes and polymerizes.



$$2CH_3CH_2CH = CH_2 \rightleftharpoons CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} — \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$$

This cracking taking place at 475°C–530°C temperature leads to *liquid phase thermal cracking*. The products are separated by fractional distillation. When the cracking oil is vaporized and then cracked at 600°C–750°C at a low pressure, it is called *vapour phase thermal cracking*. The products have better anti-knock properties.

2. *Catalytic Cracking.* The use of catalyst during cracking accelerates the reactions and at the same time modifies the yield and the nature of product. Catalyst used are synthetic composition of silica and alumina, zeolites in the form of beads or pellets.

There are two main types of catalytic cracking:

(*a*) *Fixed-bed catalytic cracking:* The catalysts are fixed in towers, through which the hot oil (500°C) flows from the top and passes down. 40% of the charge is converted to gasoline and 2–4% carbon is formed. This carbon deposits on the catalyst beds. The bottom liquid is reboiled and recycled to the fractionating column and ultimately gas oil is obtained having high octane value. The gasoline is stripped off dissolved gases and purified. The carbon deposits on the catalysts are burnt by compressed air in one chamber for reactivation while the other catalyst chambers are active (Fig. 18.7).

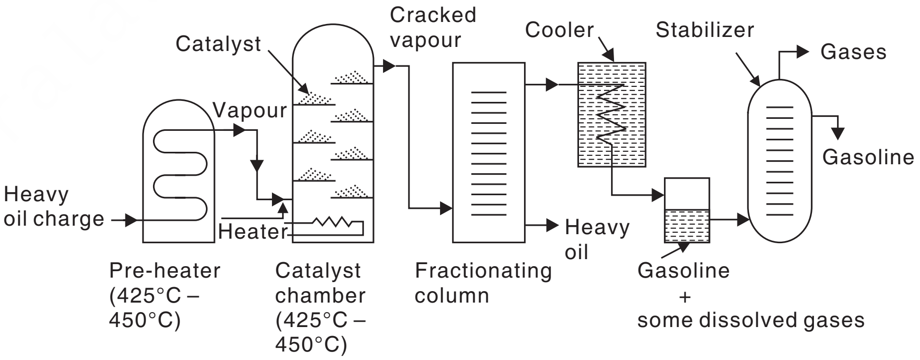


Fig. 18.7 Fixed-bed catalytic cracking.

(*b*) *Moving bed or fluidized bed catalytic cracking:* The finely powdered catalyst behaves as a fluid when suspended in gas or oil vapour. The preheated heavy oil is forced through tower along with the fluidised catalyst. At the top of the tower a cyclone separator is active to separate the cracked oil vapour and passes it to the fractionating column. The catalyst powder is retained and sent back. The catalyst becomes deactivated by a deposition, which is reactivated by burning away the deposits with compressed air in a regenerator (Fig. 18.8).

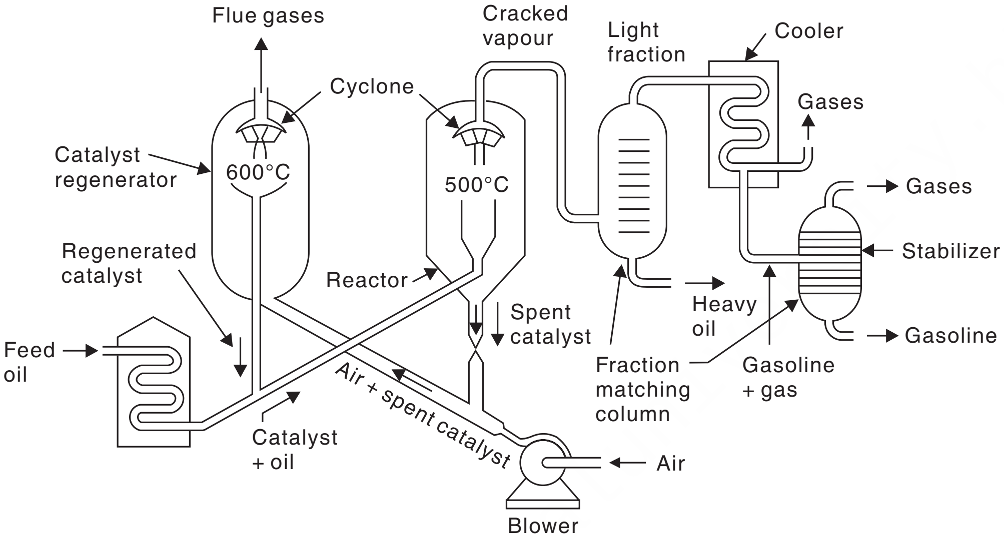


Fig. 18.8 Moving-bed type catalytic cracking.

Advantages of catalytic cracking:

(*i*) The quality and yield of petrol is better.

(*ii*) External fuel is not necessary since the coal embedded in the catalyst supplies the heat.

(*iii*) Operating pressure is lower.

(*iv*) Byproduct gas evolution being low, yield of petrol is higher.

(*v*) Due to higher aromatics content, the anti-knocking properties are higher.

(*vi*) Greater portion of S escapes as H_2S so residual S content of the oil is low.

(*vii*) Gum-forming compounds are very low.

(*viii*) In presence of specific catalysts preferentially the cracking of naphthenic materials takes place, so it becomes richer in paraffinic compounds.

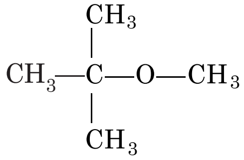
(*ix*) Only the high-boiling hydrocarbons and the side chain of the aromatics are decomposed preferentially.

Highlights:

- Gasoline is the fuel for motor engines.
- Gasoline contains alkanes C_5—C_{10} atoms.
- Enough gasoline is not produced during purified petroleum distillation.
- Oil refineries use *catalytic cracking* to make gasoline.
- For smooth running of the motors, gasoline has to burn smoothly without *knocking.*
- The octane number scale was devised by Thomas Midgley (1889-1944) and he discovered *anti-knocking* additives based on lead *i.e.*, T.E.L. (Tetra Ethyl Lead)
- Leaded fuel is now avoided and the oil companies produce high octane fuel by increasing the proportions of both branched alkanes and arenes and blending some oxygen compounds.

(*contd.*)

- The four main approaches are:
  - (*i*) *Cracking* not only makes small molecules but also forms branched chain hydrocarbons.
  - (*ii*) *Isomerisation c*onverts straight chain alkanes to branched chain by passing over Pt-catalysts.
  - (*iii*) *Reforming t*urns cyclic alkanes into arenes such as benzene and toluene.
  - (*iv*) *Addition of alcohols and ethers.* Compounds such as MTBE (Methyl Tertiary Butyl Ether) now known as 2-methoxy-2-methyl propane.



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3$$

MTBE

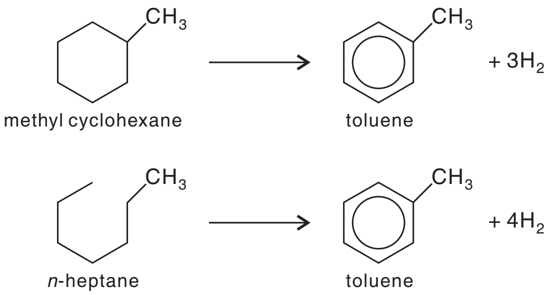
Petroleum Processing

1. *Polymerization, alkylation and isomerization.* The cracker gases in the refinery are rich in olefins. These compounds undergo polymerization either in presence of catalyst (catalytic polymerization) like phosphoric acid, H_2SO_4 or by heating at temperatures of 500°C–600°C and pressure (thermal polymerization) to yield products rich in branched-chain hydrocarbons. By this process superior quality gasolines are obtained.

$$\underset{iso\text{-butene}}{CH_3C(CH_3) = CH_2} \longrightarrow \underset{di\text{-isobutene}}{CH_3C(CH_3)_2CH_2C(CH_3) = CH_2}$$

Similarly, alkylation in presence of HF or H_2SO_4 gives *iso*-paraffins. Isomerization converts *n*-paraffins to *iso*-paraffins in presence of anhydrous $AlCl_3$ catalyst. All these processes supply excellent high volatile gasoline components.

2. *Reforming.* This process also helps in preparing high quality gasoline by heating with or without a catalyst, the naphtha fractions of gasoline. This upgrading is a result of reforming of molecules without disturbing their average molecular weights, like formation of aromatics from naphthene and paraffins.



The other reactions are the isomerization of *n*-paraffins to *iso*-paraffins and hydrocracking of higher paraffins to lower ones. Actually these aromatics and the *iso*-paraffins are the best gasoline components.

Similar to cracking, reforming is also thermal and catalytic. Thermal reforming has been almost completely replaced by catalytic reforming.

The catalysts used are molybdena, chromia supported on alumina, platinum on silica or alumina. The latter is more active, but gets poisoned easily by the impurities like S, As, N etc.

Reforming is a once through process. Fluid bed and moving bed processes are run at higher temperature and lower pressures and fixed bed processes are run at higher pressures (temperature 450°C–520°C, pressure 5–45 kg/cm^2) (Fig. 18.9).

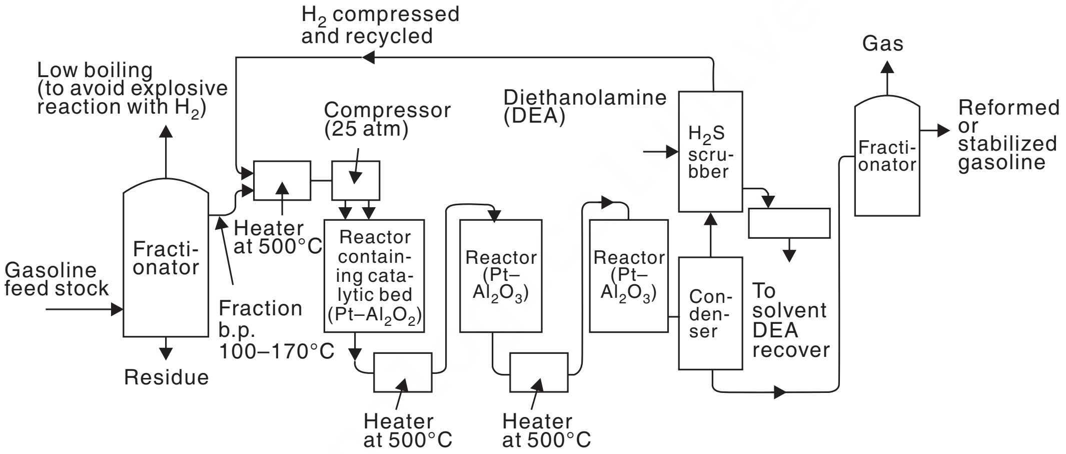


Fig. 18.9 Fixed-bed catalytic reforming process.

Refining of Gasoline

The *straight-run gasoline* obtained from the fractionation of crude petroleum contains undesirable constituents like unsaturated straight chain hydrocarbons and sulfur compounds. The former leads to gum and sludge formation and the latter leads to corrosion of engines and pollution of atmosphere. These are removed by refining processes.

(*i*) Objectionable odour forming mercaptans and H_2S make the oil sour. Oil sample treated with sodium plumbite and a little sulfur converts the sulfur compounds into disulfides (*Doctor's process*). The black PbS precipitates and the other disulfides are extracted with a suitable solvent, rendering the foul smelling stock to sweet smelling or odourless stock and the process is called *sweetening process.*

$$2RSH + Na_2PbO_2 \longrightarrow Pb(RS)_2 + 2NaOH$$

$$Pb(RS)_2 + S \longrightarrow PbS + \underset{\text{disulfide}}{RSSR}$$

(*ii*) Gasoline is percolated through "Fuller's earth" which absorbs the olefins and coloring matters present in it.

(*iii*) The storing quality of the refined gasoline is improved by adding different inhibitors of oxidations to it.

(*iv*) Refined gasoline is blended with suitable fractions of catalytically cracked gasoline to impart good combustion qualities.

Knocking

Octane Number. Maximum power is derived from gasoline when it burns silently and uniformly in an internal combustion engine. Due to presence of certain constituents in the gasoline, the rate of oxidation sometimes becomes so great that the unburnt fuel may burn rapidly with the formation of explosive violence. This is known as *knocking*. Knocking results in loss of efficiency of the engine and also leads to its short life.

The anti-knock quality of a fuel is expressed as its octane number.

Octane number is equal to the percentage by volume of iso-octane (2,2,4-trimethyl pentane) in a mixture of *n*-heptane and iso-octane having the same knocking tendency compared to the sample of gasoline being tested; iso-octane has the best antiknocking properties and assigned an octane number of 100 whereas *n*-heptane has poor antiknocking property and assigned an octane number of zero. The hydrocarbons present influence the knocking properties of gasoline which vary according to the series: straight chain paraffin > branched chain paraffin > olefin > cycloparaffin > aromatics. The fuel which has same knocking tendency with the mixture having 80% *iso*-octance has octane number 80.

The most effective antiknock agent added is tetraethyl lead (TEL) along with ethylene dibromide which prevents the deposition of lead by forming volatile lead halides. Other antiknocking agents are tetramethyl lead (TML), tertiary butyl acetate, diethyl telluride.

1.0–1.5 ml of TEL is added per litre of petrol. TEL functions by being converted to a cloud of finely divided lead oxide particles, which react with any hydrocarbon peroxide molecules formed in the engine cylinder thereby solving down the chain oxidation reaction and preventing knocking.

Cetane Number

There is a delay period between the injection of diesel fuel and its ignition. This delay period if becomes large, too much fuel accumulates in the cylinder and burn very rapidly and causes "diesel knock". This delay period is connected to the type of hydrocarbons present in the diesel. Increasing delay period occurs in the series: *n*-paraffins < olefins < naphthenes < isoparaffins < aromatics. The order is the reverse for gasoline anti-knock quality. *n*-hexadecane is given cetane number 100 and α-methyl naphthalene given cetane number zero. If a given fuel matches in quality with the blend having 40/60 blend of cetane and α-methyl naphthalene, it is assigned a cetane number 40. The cetane number of diesel can be improved by adding amyl/butyl nitrate, carbamates, ditertiary butyl peroxide and metal organic compounds.

Liquid Fuel from Coal and Coal Tar

The conversion of coal into oil is essentially raising the H:C ratio.

1. ***Bergius-Pier Process:*** Destructive hydrogenation of coal in presence of a catalyst yields oil, but it is not yet competitive with petroleum refining.

Coal is ground and made into a paste with a heavy recycle oil and a catalyst like iron, tin or molybdenum compound. The paste is preheated and treated with H_2 at 250–350 atm. pressure and 450°C–500°C temperature. The unreacted coal is filtered-off and the liquid product distilled. Hydrogen combines with coal to form saturated hydrocarbons, which decompose at high temperature yielding low-boiling hydrocarbons. The crude oil is fractionated to get (*i*) gasoline (*ii*) middle oil and (*iii*) heavy oil which is recycled. Middle oil is hydrogenated in vapour phase with catalyst to yield more gasoline. Yield of gasoline is 60% of the coal dust.

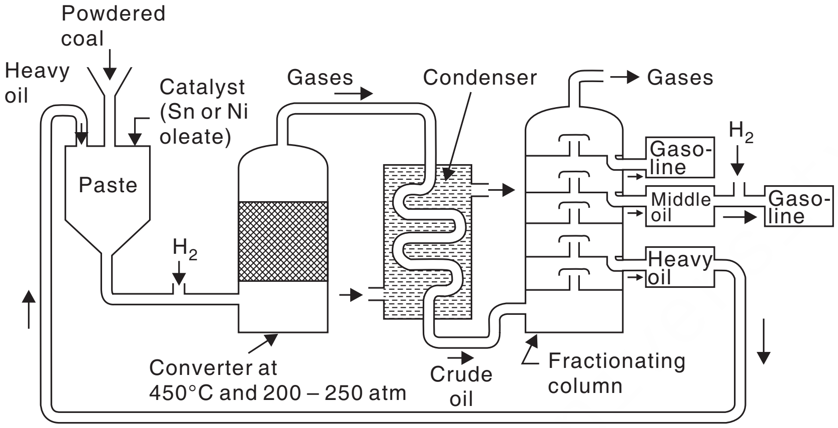


Fig. 18.10 Bergius process of hydrogenation of coal to gasoline.

2. ***Fischer-Tropsch Process.*** The process is based on the catalytic hydrogenation of carbon monoxide leading to the following reaction:

$$nCO + (2n + 1)H_2 \longrightarrow \underset{\text{Paraffin}}{C_nH_{2n+2}} + H_2O$$

$$nCO + 2nH_2 \longrightarrow \underset{\text{Olefin}}{C_nH_{2n}} \longrightarrow C_nH_{2n} + nH_2O$$

Water gas ($CO + H_2$), produced by passing steam over heated coke is mixed with hydrogen.

The gas is purified by passing over Fe_2O_3 to remove H_2S, then passing over a mixture of $Fe_2O_3.Na_2CO_3$ to remove organic sulfur compounds. The purified gas is compressed to 5 to 25 atm. at 200°C–300°C passed through a converter containing catalyst which is a mixture of 100 parts cobalt, 5 parts thorium, 8 parts magnesium and 200 parts keiselguhr.

The exothermic reaction leads to the formation of straight-chain saturated and unsaturated hydrocarbons. The crude oil on fractionation yields (*i*) gasoline and (*ii*) heavy oil, which are cracked to yield more gasoline.

The gasoline contains straight chain hydrocarbons and hence have low octane number, so needs reforming before use (Fig. 18.11).

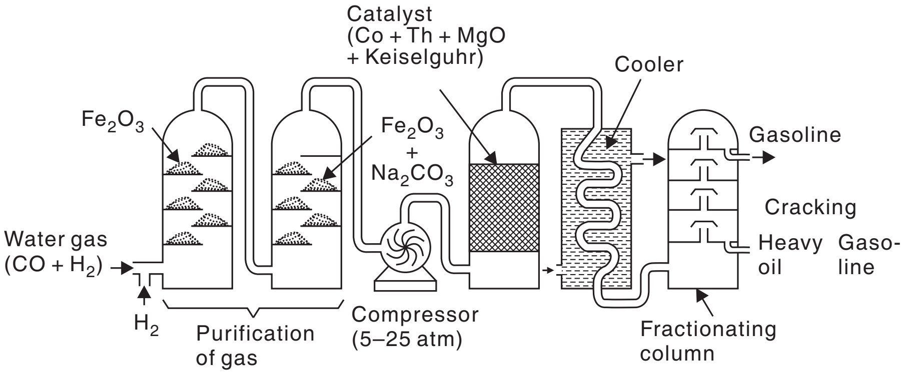


Fig. 18.11 Fisher-Tropsch method.

Important Petroleum Products

The main products of refinery are motor and aviation gasoline, kerosene, diesel fuel, fuel oils; other products include lubricating oils, wax, bitumen, coke, LPG etc.

Gasolines. It is used in reciprocating spark-ignition internal combustion engines.

Motor gasoline is a mixture of low boiling hydrocarbons (215°C) and made by blending—

(*i*) Straight run gasoline (direct distillation of crude oil), (*ii*) cracked gasoline, (*iii*) reformed naphtha and other fractions, 10% butane for easy starting of engines, TEL and other additives. Colours are added to identify different grades.

Aviation gasolines have higher volatility and higher percentages of TEL and isoparaffin.

Kerosene. Kerosene is used for domestic purpose, space heaters for jet engines. It is obtained as a straight-run distillate from crude oils. No additives are required. Purification involves removal of sulphur.

Diesel fuel. Diesel fuels are prepared from heavy distillate obtained from catalytic cracking units. It is rich in aromatics and *iso*-paraffins, the low cetane number is improved by additives. Volatility is improved by blending with light fractions. In a high-speed diesel engine, the cetane numbers should be more than 45 whereas for low speed engines it should be in the range of 25 to 35.

Fuel oils. Wide range of liquid fuels used in boilers and furnaces are covered by this term. Cycle gas oil is the light variety and needs a number of treatments for purification. The heavy fuel oil produced from the cracking units are the heavy variety.

LPG. Liquefied petroleum gas is obtained as a byproduct during the cracking of heavy oils or from natural gas. LPG contains hydrocarbons which are gaseous under atmospheric pressure but can be liquefied under pressure. They are *n*-butane, isobutane, butylene, propane etc. It is used as domestic and industrial fuels and in future it may be used as motor fuel.

Non-petroleum Fuels

1. *Benzol.* Refined benzol is essentially a mixture of 70% benzene, 18% toluene and 6% xylenes. Its octane rating ranges between 87 and 90. It is a good fuel for internal combustion engines but its initial boiling point is high (80°C), so it can be used only when blended with gasolines. The other defect is its high freezing point (55°C), so it cannot be used in cold countries.

Alcohols. Methyl and ethyl alcohols can be used in gasoline engines. Cost considerations prohibit their use. Octane number is high as 114 and 99, respectively. But their calorific values are low. Ethyl alcohol is not used as a prime fuel but used as blends with gasoline upto 25% alcohol and the mixture is called “gasohol”. It serves to increase the octane rating.

The importance of ethyl alcohol as a fuel lies in the fact that it can be produced from naturally available carbohydrates by fermentation. It requires about 36 hrs. to complete whereby the fermented liquid contains 18-20% alcohol which is then fractionally distilled to recified spirit containing 90-95% alcohol, from which absolute alcohol can be obtained after treatment with lime and distillation.

GASEOUS FUELS

(*a*) Fuel gas from nature:
  (*i*) Natural gas
  (*ii*) Methane from coal mines.
(*b*) Fuel gas from solid fuels:
  (*i*) Producer gas
  (*ii*) Water gas
  (*iii*) Coal gas
  (*iv*) Blast furnace gas
(*c*) Fuel gas from petroleum:
  (*i*) Refinery gases
  (*ii*) LPG
  (*iii*) Gases from oil gasification.
(*d*) Fuel gas made by fermentation of organic wastes.

Natural Gas

Natural gas is a mixture of paraffinic hydrocarbons and methane is the principal component. Natural gas when found to occur with petroleum in oil wells is called ‘wet gas’ and when it is associated with crude oil the gas is called ‘dry gas’. Water, dirt, H_2S, CO_2, N_2 and heavier hydrocarbons are removed from the gas and finally it contains from 50 to 95% methane, 5-10% ethane, 3% H_2 etc. The calorific value is 12,000–14000 kcal/m^3.

Natural gas is used (*i*) as a domestic fuel, (*ii*) for manufacture of various chemicals (*iii*) as raw material for the manufacture of H_2 and carbon black and (*iv*) for synthetic protein preparation from methane.

Coal Gas

Coal is produced by the high temperature carbonisation of coal in gas retorts and coke ovens. Its calorific value is around 5000 kcal/m^3. It contains 40% H_2, 32% CH_4, 7% CO, 2% C_2H_2, 3% C_2H_5, 4% N_2 and 1% CO_2. It burns with a long smoky flame.

The coke oven gas is purified in steps to obtain the coal gas finally. Tar and ammonia are first removed by cooling the gas and water scrubbing, then benzol, naphthalene are removed by creosote oil scrubbing, H_2S is finally removed by passing it over moist ferric oxide.

$$2Fe(OH)_3 + 3H_2S \longrightarrow Fe_2S_3 + 6H_2O$$

Coal gas is used (*i*) for illuminating towns and cities, (*ii*) as a fuel, (*iii*) as a raw material for NH_3 production and (*iv*) in metallurgical operations to provide reducing atmosphere.

Producer Gas

It is a mixture of combustible gases like CO and H_2 and large amount of non-combustible gases like N_2, CO_2 etc. It is prepared by passing air and steam over an incandescent bed of solid carbonaceous fuel in a reactor called “gas producer” or simply a “producer”. It is a fuel of low calorific value (1300 kcal/m^3) but its advantage is its cheapness and ease of production. The carbonaceous fuel used is generally coal or coke, though wood waste, peat etc. can be used.

The gas producer consists of a steel vessel with inner lining made up of refractory bricks. The dimension of the vessel is about 4 m height and at the top there is a cone feeder and a side opening for producer gas outlet. At the base there is inlets for air and steam and an outlet for the ash.

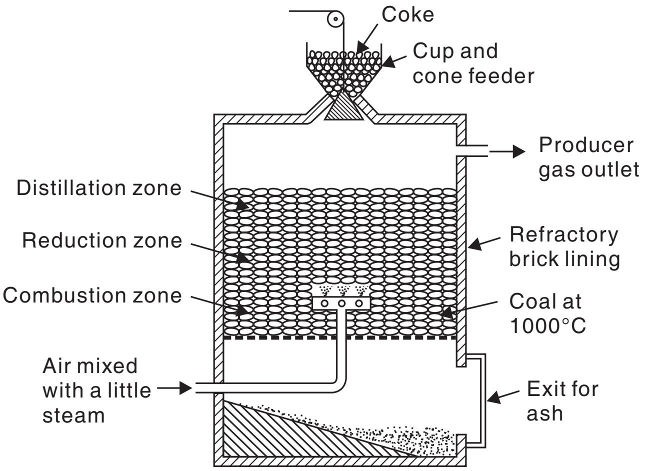


Fig. 18.12 Gas producer.

Reaction Zones in a Gas Producer

(*a*) **Ash zone.** The fuel bed in a normal producer is on metallic grate. The air-steam blast is preheated by the ash zone which also protects the grate from intense heat.

(*b*) **Oxidation zone.** This is just next to the ash zone. The oxygen is consumed within 75 to 100 mm of the bed, which constitutes the zone. CO_2 forms at the expense of O_2. Its concentration reaches a maximum at the top when CO begins to appear. The temperature at this zone is about 1100°C.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$
$$C + \frac{1}{2} O_2 \longrightarrow CO + 29.5 \text{ kcal}$$

(*c*) **Reduction zone.**

$$CO_2 + C \longrightarrow 2CO - 36 \text{ kcal}$$
$$C + H_2O \longrightarrow CO_2 + H_2 - 29 \text{ kcal}$$
$$C + 2H_2O \longrightarrow CO_2 + 2H_2 - 19 \text{ kcal}$$

As long as O_2 is in excess, CO_2 is formed, which then undergoes reduction into CO and the reaction is endothermic and is called Bondonard reaction. Its equilibrium constant greatly increases with rise in temperature. Other reactions are also endothermic, where red hot coke, combines with steam to liberate H_2 and from oxides of C. The temperature is around 1000°C (*d*) The uppermost layer of the bed is the *drying and carbonisation zone.* The water vapor and the volatile matter are added to the escaping gas which results in production of enriched gases. The topmost zone serves to preheat the precarbonised fuels coming in. The temperature of this zone is from 400°C-800°C. The average composition of the producer gas is CO: 22-30%, H_2: 8-12%, N_2: 52-55%, CO_2: 3%.

Producer gas is used for heating the furnaces for the production of steel and glass, muffle furnaces for coal gas production, and in metallurgical operations.

For the production of producer gas, only air can be used, steam used along with air is advantageous since (*i*) it raises the content of combustible components (CO + C_2) compared to noncombustible thereby increasing calorific value, (*ii*) the endothermic reaction of steam and C prevents localised overheating of a fuel bed and leads to diminished clinker formation.

Water Gas

Water gas is a gaseous fuel of medium calorific value (2800 kcal/m^3) generated by gasifying solid incandescent source of carbon in superheated steam. The equipment is known as water gas generator and is more or less similar to that shown in Fig. 18.12 where the following reaction takes place which is endothermic

$$C + H_2O \longrightarrow CO + H_2 - 29 \text{ kcal}$$

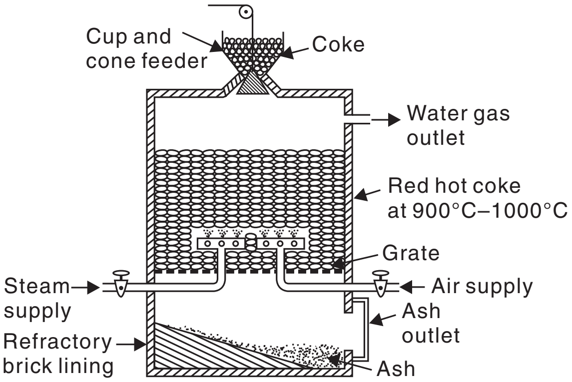


Fig. 18.13 Water gas production.

This gas burns with a blue flame owing to high carbon monoxide content and hence known as blue water gas. The bed of coke in the reactor is at 1400°C to 1000°C. As the reaction is endothermic temperature gradually falls and when it comes to 1000°C the blast of steam is stopped and air blast is passed and the following exothermic reactions occur.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$
$$2C + O_2 \longrightarrow CO + 59 \text{ kcal}$$

The reaction again rises and these cycles alternately take place to maintain the temperature. After the production, ash is removed and the generator recharged. The water gas passing through the superheater is cooled and then purified.

The average composition is H_2: 51%, CO: 41%; N_2: 4%, CO_2: 4%

Blue water gas is used as a source of hydrogen, as a fuel gas.

The calorific value of water gas can be enhanced by adding gaseous hydrocarbons (obtained from cracking crude oils) to get *carburetted water gas* (Calorific value 4500 kcal; $CO_2 \rightarrow 3\%(m^3)$); composition of carburetted water gas is 35% H_2, 25% CO, 35% saturated and unsaturated hydrocarbons and 5% $N_2 + CO_2$.

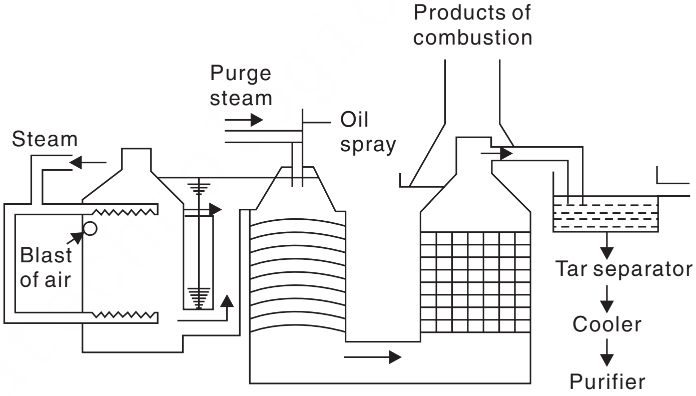


Fig. 18.14 Manufacture of carburetted water gas.

Biogas Production

Aquatic plants, organic wastes from domestic, agricultural and industrial sectors with high B.O.D. value (Feed stock) are digested anaerobically to produce *biogas*. The biogas is totally used as fuel. The chief constituent of biogas is methane, so the process is also called *biomethanation*. Composition of biogas is given below:

Component	*Volume%*
CH_4	52-95
CO_2	9-45
H_2S	0.001-2
H_2	0.01-2
N_2	0.1-4
O_2	0.02-6.5
CO	0.001
NH_3	Small

Conditions for Biomethanation

- Temperature = 35°
- pH = 6.8-8.2
- Anaerobic condition.
- Trace elements = Na^+, Co^{+3}, Ni^{+2} etc.

Arrangements for Biomethanation

Feed stock is mainly cowdung.

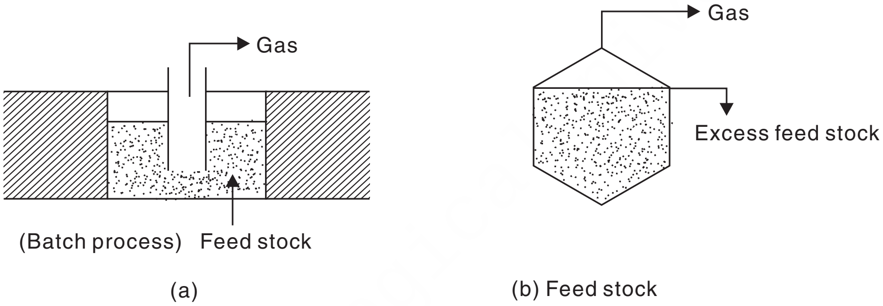


Fig. 18.15

Better quality of coal should have low nitrogen and sulphur content. Higher percentage of oxygen is also undesirable as an increase in 1% oxygen content decreases the calorific value by about 1.7%.

Method of Analysis of Flue Gas

Analysis of flue gas will indicate the complete or incomplete combustion of a fuel; which is very essential in respect of efficient utilization of the fuel. The analysis is done in Orsat's apparatus and is based on the principle of absorption of

- CO_2 in KOH solution (500 gl^{-1}, 500 ml)
- O_2 in alkaline pyrogallic acid (25 g of pyrogallic acid in 400 gl^{-1} KOH solution, 500 ml)
- CO in ammoniacal cuprous chloride solution (100 g Cu_2Cl_2 + 125 ml liquor ammonia + Rest water to make up the volume, 500 ml).

Description of the Apparatus

It consists of a water jacketted measuring burette, connected in series with the absorption bulbs containing the above three solutions successively as depicted in the Fig. 18.16. The water jacket maintains the temperature of the gas constant. The absorption bulbs are filled with glass tubes for better absorption of the gases.

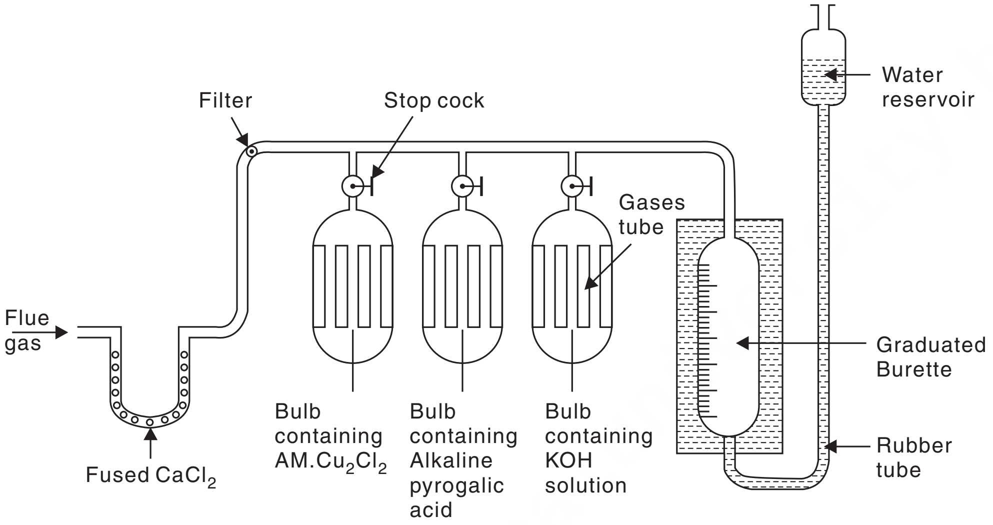


Fig. 18.16

Procedure

- The apparatus is tested for its air-lightness.
- The flue gas (100 ml) is taken in the apparatus in the measuring burette by adjusting the volume by water reservoir atmospheric pressure.
- The stopper (1) is opened for CO_2 absorption and water reservoir is raised to force the gas inside the bulb. The gas is finally taken in the burette and the volume of the gas is measured by making the levels of water inside the burette and water reservoir equal. The decrease in volume gives the percentage by volume of CO_2 in the flue gas.
- The stopper (2) is opened and provided as usual to get the percentage by volume of O_2 in the flue gas.
- The stopper (3) is opened and proceeded as usual to get the percentage by volume of CO in the gas.
- The sequence of the bulbs should be strictly followed.

Implications of the Analysis

- If the flue gas contains greater percentage of CO it is implied that considerable wastage of fuel is taking place due to incomplete combustion and the O_2 supply is insufficient.
- The greater percentage of O_2 in the flue gas indicates that O_2 supply is in excess.
- Result of the analysis will help to control the combustion process.

SOLVED EXAMPLES

Example 1. *A sample of coal contains:*

$$C = 93\%, H = 6\% \text{ and ash} = 1\%$$

Calculate the gross and net calorific V value of the coal from the following data:

Weight of coal burnt (m) = 0.92 g

Weight of water taken (w) = 550 g

Water equivalent of bomb calorimeter (W) = 2,200 g.

Rise in temperature $(t_2 - t_1) = 2.42°C$; *Fuse wire correction = 10 cal.*

$L = 580\ cal/g^{-1}$.

Sol.

$$\text{HCV} = \frac{(\text{W} + w)\,(t_2 - t_1) - [\text{acid} + \text{fuse}]\ \text{correction}}{m}$$

$$= \frac{(2{,}200 + 530) \times 2.42 - [50 + 10]}{0.92}\ \text{cal/g}^{-1}$$

$$= \mathbf{7168.5\ cal/g}$$

Net Calorific Value (NCV)

$$= (\text{HCV} - 0.09\ \text{H} \times \text{L})\ \text{cal/g}^{-1}$$

$$= (7168.5 - 0.09 \times 6 \times 580)\ \text{cal/g}^{-1}$$

$$= \mathbf{6{,}855.3\ cal/g.}$$

Example 2. *A sample of coal was analysed as follows:*

Exactly 2.5 g was weighed in a silica crucible, after heating for 1 hr. at 110°C the residue was weighed to be 2.415 g. Next the crucible was covered with a rented lid and strongly heated for exactly 7 mins. at 1000°C. The residue was weighed to be 1.528 g. Then the crucible was heated without cover until a constant weight to 0.245 g was obtained. From the above data calculate the proximate analysis of coal.

Sol. Moisture in the sample = (2.5 – 2.915)g = 0.085 g

So, % moisture = $\frac{0.085}{2.5} \times 100 = 3.4$

So, amount of volatile carbonaceous matter (VCM) in the sample = (2.415 – 1.528) g = 0.887 g.

So, % $\quad \text{VCM} = \frac{0.887 \times 100}{2.5} = 35.48\%$

$$\%\ \text{Ash} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100$$

$$= \frac{0.245}{2.5} \times 100 = 35.48\%$$

Fixed carbon = (1.528 – 0.245)g = 1.283 g

% Fixed carbon $= \frac{1.283 \times 100}{2.5} = 51.32\%.$

Example 3. *On burning 0.83 g of a solid fuel in bomb calorimeter, the temperature of 3,500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385 g and 587 cal/g, respectively. If the fuel contains 0.77% H, calculate HCV and NCV.*

Sol.

$$\text{HCV} = \frac{(\text{W} + w)\,(t_2 - t_1)}{m}$$

$$= \frac{(385 + 3500)\,(29.2 - 26.5)}{0.83} = 12638\ \text{cal g}^{-1}$$

$$\text{NCV} = (\text{HCV} - 0.09\ \text{H} \times \text{L})\ \text{cal g}^{-1}$$

$$= (12638 - 0.09 \times 0.7 \times 587)\ \text{cal g}^{-1} = 12601\ \text{cal g}^{-1}.$$

Example 4. *An ultimate analysis of 1 g coal for nitrogen (N) estimation is the Kjelldahl method, the evolved* NH_3 *has collected in 25 ml* $\left(\frac{N}{10}\right)$ H_2SO_4 *acid solution. To neutralise the excess acid, 15 ml of 0.1 (N) NaOH was required. Calculate the % of nitrogen in the given sample.*

Sol. In the Kjelldahl method organic compounds containing nitrogen are heated with concentrated H_2SO_4 to convert to $(NH_4)_2SO_4$. This $(NH_4)_2SO_4$ during soiling with alkali liberates NH_3 that is absorbed in $H_2SO_4\left(\frac{N}{10}\right)$. Excess acid is titrated with NaOH.

The volume of H_2SO_4 consumed by NH_3 $(25 \times .1 - 15 \times .1)$ ml (N) = 1 ml (N)

Now, 100 c.c(N) $H_2SO_4 \equiv 17$ g $NH_3 \equiv 14$ g N.

$$\therefore \quad 1 \text{ c.c(N) } H_2SO_4 = \frac{14}{1000} \text{ gN} = 0.014 \text{ gN}$$

Again 0.014 g Nitrogen is present in 1 g coal.

So, % of N in the coal sample $= \frac{0.014}{1} \times 100 = 1.4\%$.

Example 5. *A gaseous fuel has the following composition of volume:*

$$H_2 = 24\%;\ CH_4 = 30\%;\ C_2H_6 = 11\%,$$
$$C_2H_4 = 4.5\%;\ C_4H_8 = 2.5\%;\ CO = 6\%;\ CO_2 = 8\%;$$
$$O_2 = 2\% \text{ and } N_2 = 12\%.$$

Calculate (i) air to fuel ratio and (ii) volume of dry products of combustion using 40% excess air.

Sol. Basis: 1 m^3 of gaseous fuel.

Volume of combustible gases (m^3)	*Reaction*	*Volume of O_2 m^3*	*Volume of products of combustion on dry basis (m^3)*
$H_2 = 0.24$	$H_2 + \frac{1}{2}O_2 = H_2O$	$0.24 \times \frac{1}{2} = 0.12$	–
$CH_4 = 0.30$	$CH_4 + 2O_2 = CO_2 + 2H_2O$	$0.3 \times 2 = 0.60$	$CO_2 = 0.3$
$C_2H_6 = 0.11$	$C_2H_6 + 3\frac{1}{2}O_2 = 2CO_2 + 3H_2O$	$0.11 \times \frac{7}{2} = 0.385$	$CO_2 = 0.11 \times 2 = 0.22$
$C_2H_4 = 0.045$	$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	$0.045 \times 3 = 0.135$	$CO_2 = 0.045 \times 2 = 0.09$
$C_4H_8 = 0.025$	$C_4H_8 + 6O_2 = 4CO_2 + 4H_2O$	$0.025 \times 6 = 0.15$	$CO_2 = 0.025 \times 4 = 0.1$
$CO = 0.06$	$CO + \frac{1}{2}O_2 = CO_2$	$0.06 \times \frac{1}{2} = 0.03$	$CO_2 = 0.06 \times 1 = 0.06$
		Total = 1.42 m^3 Less = 0.02 m^3	Total = 0.77 m^3 CO_2 in fuel = 0.08 m^3
		Net need = 1.4 m^3 (O_2)	Net CO_2 = 0.85 m^3

Volume of air required (when 40% excess)

$$1.4 \times \frac{100}{21} \times \frac{140}{100} = 9.333 \text{ m}^3$$

$\therefore$ air: fuel = 9.333:1 ...(*i*)

Total volume of dry products = $CO_2 + N_2$ (from fuel + air) + O_2 (excess)

$$= 0.85 + \left[0.12 + \left(\frac{79 \times 9.33}{100}\right)\right] + \left(9.33 \times \frac{21}{100} - 1.4\right) \text{m}^3 = 8.782 \text{ m}^3$$

Composition of product of combustion on dry basis.

$$CO_2 = \frac{0.82 \times 100}{8.782} = 9.337\%$$

$$N_2 = \frac{7.373 \times 100}{8.782} = 83.95\%$$

$$O_2 = \frac{.559 \times 100}{8.782} = 6.365\%.$$

Example 6. *Calculate the volume of air required for complete combustion of 1 m*^{3} *of a gaseous fuel having the composition*

$CO = 46\%$, $CH_4 = 10\%$; $H_2 = 40\%$

$C_2H_2 = 2\%$; $N_2 = 1\%$ *and the remaining being* CO_2.

Sol. Basis: 1 m^3 of the gaseous fuel.

Combustible gases in the fuel (m^3*)*	*Reaction*	*Volume of* O_2 *required (m*^{3}*)*
$CO = 0.46$	$CO + \frac{1}{2} O_2 = CO_2$	$0.46 \times \frac{1}{2} = 0.23$
$CH_4 = 0.10$	$CH_4 + 2O_2 = CO_2 + 2H_2O$	$0.1 \times 2 = 0.20$
$H_2 = 0.4$	$H_2 + \frac{1}{2} O_2 = H_2O$	$0.4 \times \frac{1}{2} = 0.20$
$C_2H_2 = 0.02$	$C_2H_2 + 2\frac{1}{2} O_2 = 2CO_2 + H_2O$	$0.02 \times \frac{5}{2} = 0.05$
		Total $O_2 = 0.68$ m^3 required

As air contains 21% of O_2 by volume

$\therefore$ Volume of air required $= \left(0.68 \times \frac{100}{21}\right) \text{m}^3 = 3.238 \text{ m}^3$.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is a coke?

Ans. It is a carbonaceous residue obtained from the destructive distillation of coal, petroleum and coal tar pitch. Petroleum yields coke during cracking processes. The main source of coke is coal. Petroleum coke is used as metallurgical coke since it is pure.

Q. 2. What is a fluidised bed?

Ans. Finely divided solids suspended in a moving gas or liquid behave like a fluid. Catalyst in this form is used for catalytic cracking.

Q. 3 What is petroleum?

Ans. It is a highly complex mixture of paraffinic, cycloparaffinic (naphthenic) and aromatic compounds with traces of N, O and low percentage of S and is obtained from underground.

Q. 4. What is Naphtha?

Ans. It is a refined petroleum product 90% of which distils below 240°C and 10% distils below 175°C. It is obtained by cracking of petroleum and mainly used as thinners for paints and varnishes.

Q. 5. What is flash point?

Ans. It is the lowest temperature at which the vapour of a volatile liquid or solid gets ignited by a small flame *e.g.,* flash point of kerosene is 90°F.

Q. 6. What is an anti-knocking agent?

Ans. They are organometallic compounds that increase the octane number of gasoline when added in low percentage to it. Most common is TEL (-tetraethyl lead). They can increase the octane number over 100%.

Q. 7. What are Octane Number and Cetane Number?

Ans. See text page 396.

Q. 8. What is aviation gasoline?

Ans. It is a variety of gasoline having high octane number *i.e.,* 100 and high volatility and hence used for aircraft. The main components of aviation gasoline are isoparaffins and some TEL.

Q. 9. What is straight run gasoline?

Ans. Gasoline obtained by direct distillation of petroleum without using other conversion processes like cracking is known as straight run gasoline. Its octane number is low.

Q. 10. (a) What is LPG? (b) What is LNG?

Ans. (*a*) LPG or Liquefied petroleum gas is obtained from 'Wet Natural gas' from underground, by washing it with gas oil and fractionating the useful fraction.

(*b*) LNG is Liquefied Natural gas.

Q. 11. What is reforming?

Ans. See text page 395.

Q. 12. What is the difference between gross and net calorific values?

Ans. See text page 378.

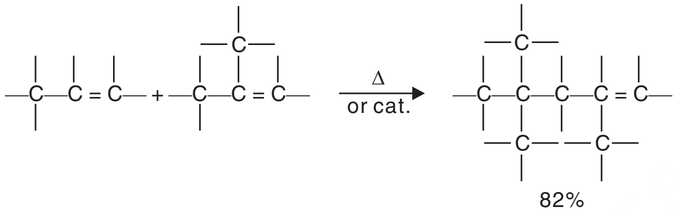
Q. 13. Mention the basic reactions or conversion processes for petrochemical industry.

Ans. Petroleum offers a fertile field both for gasoline and for petrochemicals. The following examples are a few of the more important basic reactions.

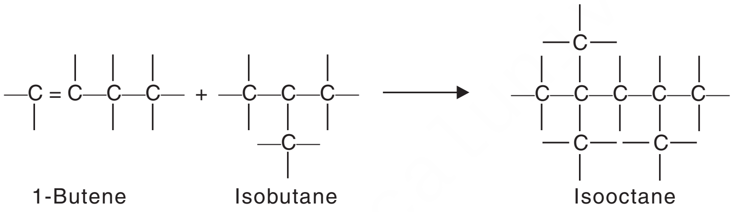
- *Cracking*

$$C_7H_{15}.C_{15}H_{30}.C_7H_{15} \xrightarrow{\Delta} \underset{\text{gasoline}}{C_7H_{16}} + \underset{\text{antiknock gasoline}}{C_6H_{12} = CH_2 + C_{14}H_{28} = CH_2}$$

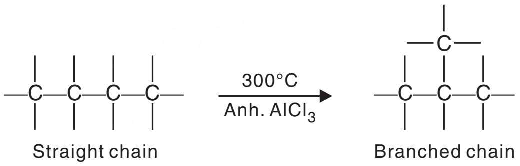
- *Polymerisation*



- *Alkylation*

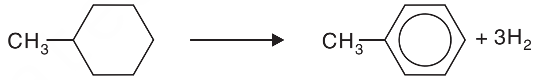


- *Isomerisation*

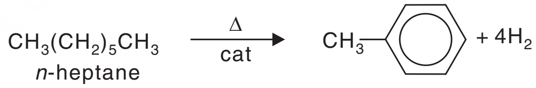


- *Hydroforming or Aromatisation*

(*i*)



(*ii*)



Q. 14. What is Benzol?

Ans. Benzol is a coal tar distillation fraction (b.p. 70-150°C) containing 70% benzene, 18% toluene and 6% xylenes. It is blended with petrol. It has octane rating 87-90. The blended petrol is a good motor fuel.

Q. 15. What is power alcohol?

Ans. Ethyl alcohol when blended with petrol to be used as a fuel for internal combustion engine, is known as power alcohol.

Q. 16. What is gasohol?

Ans. It is a mixture of gasoline and alcohol.

gasoline + alcohol = gasohol.

The use of grain alcohol as a blending agent with petrol is a controversial issue in the world. Though blending will reduce 10% petrol consumption but alochol production by fermentation will make use of food grains which is not desirable. Moreover, rectified spirit (95% alcohol) is not suitable for blending, 99.5% alcohol is to be produced which will make the cost higher. That is why now-a-days butanol is tried for the purpose.

Q. 17. What is oil gas?

Ans. Oil gas is mainly obtained by cracking of kerosene oil. But other oils like diesel and heavy oils and petrol may also be used for cracking. A device is set up where a plate is heated specially electrically and the oil is allowed to drop on the hot plate. The oil is cracked to lower gaseous hydrocarbons.

$$C_{12}H_{26} \longrightarrow CH_4 + C_2H_6 + C_2H_4 + C_2H_2 + \text{etc.} + \text{tar}$$

The resulting gases are passed generally through a hydraulic main and collected in a gas holder by displacement of water.

The composition of oil gas is

CH_4 = 25-30%, H_2 = 50-55%, CO = 10-12%, CO_2 = 3%,
Calorific value = 54000 kcal/m^3.

The gas is mainly generated for laboratory use.

Q. 18. What are the advantages of a gaseous fuel?

Ans.

- Can be distributed over a wide area by pipeline.
- Smooth combustion without smoke and ash.
- The temperature of heating can be controlled by controlling the gas flow to the burner.
- Higher calorific values.

Q. 19. Mention the disadvantages of a gaseous fuel.

Ans.

- Danger of explosion
- Larger scale fire risk.

Q. 20. What is an anti-knocking agent?

Ans. The organometallic compounds like TEL or TML, which increase octane number of a fuel.

Q. 21. What is an aviation gasoline?

Ans. The variety of gasoline specially suitable for aircraft having octane number well over 100.

Q. 22. Why is sulphur content controlled below 0.1%?

Ans. Sulphur and sulphur compounds greatly reduce effectiveness of TEL to increase the octane number of a fuel.

Q. 23. What is a natural gasoline?

Ans. A mixture of butane, pentane, and hexane obtained from natural gas.

Q. 24. What is HDA process?

Ans. Gasoline produced, for the manufacture of ethene, as a byproduct is known as pyrolysis gasoline. This gasoline is mainly used to produce benzene by Hydro-DeAlkylation (HDA) process.

$$CH_3(CH_2)_8CH_3 \xrightarrow{700\text{ K}} \underset{\text{octane}}{C_8H_{18}} + \underset{\text{ethene}}{CH_2 = CH_2}$$

$$C_8H_{18} \xrightarrow{\text{HDA}} C_6H_6$$

Q. 25. What is white gasoline?

Ans. It is unleaded gasoline used for motor boats.

Q. 26. Why is calorific value of coal gas higher than that of producer gas?

Ans. Coal gas contains all the combustible gases like CH_4, C_2H_4, C_2H_2, CO and H_2, whereas producer gas contains CO, H_2 and N_2. N_2 acts as inert diluent.

So calorific value of coal gas is higher than that of producer gas.

Q. 27. Producer gas is made by passing air and steam through a thick bed of coal. Why?

Ans. The primary purpose of steam is to use up the heat developed during exothermic reaction of coal and O_2 of air to maintain the temperature of producer.

Q. 28. Why is NCV greater than GCV?

Ans. Gross calorific value GCV includes the latent heat steam during combustion of a fuel, but Net calorific value NCV excludes the latent heat of steam.

Q. 29. Why a good solid fuel must have low ash content?

Ans. Ash is inorganic in nature. So high ash content decreases the calorific value of a fuel.

Q. 30. What is CNG?

Ans. CNG is compressed natural gas used in motor engines now-a-days instead of gasoline fuel causing less pollution.

Q. 31. What is synthesis gas or syn gas?

Ans. Modern processes produce a mixture of CO and H_2 from coal and steam more efficiently than the old water gas and producer gas plants. Two varieties of gas are obtained: (*i*) *Low heat gas* (*ii*) *Medium heat gas*. Low heat gas contains 50% N_2. These gases are known as synthesis or syn gas. The gasification is done in fixed bed: (*i*) Fluidised bed.(*ii*) Entrained bed.

Reactions:

(*i*) $C + H_2O = CO + H_2$

(*ii*) $CO + H_2O = CO_2 + H_2$

(*iii*) $C + CO_2 = 2CO$

Q. 32. What is SNG (Substitute Natural Gas)?

Ans. (*i*) During the production of syn gas, at sufficiently high pressure *i.e.*, during hydrogasification H_2 liberated converts carbon to CH_4.

$$C + 2H_2 = CH_4,\ CO + 3H_2 \xrightarrow{\text{cat}} CH_4 + H_2O$$

The gas produced was known as synthetic natural gas. But the synthetic product cannot be known as natural; so now it is called substitute natural gas (SNG). The operating pressure may be atmospheric to 7 MPA and temperature 800°C-1650°C for gasification. The higher pressure and lower temperature result in the formation of larger amount of SNG.

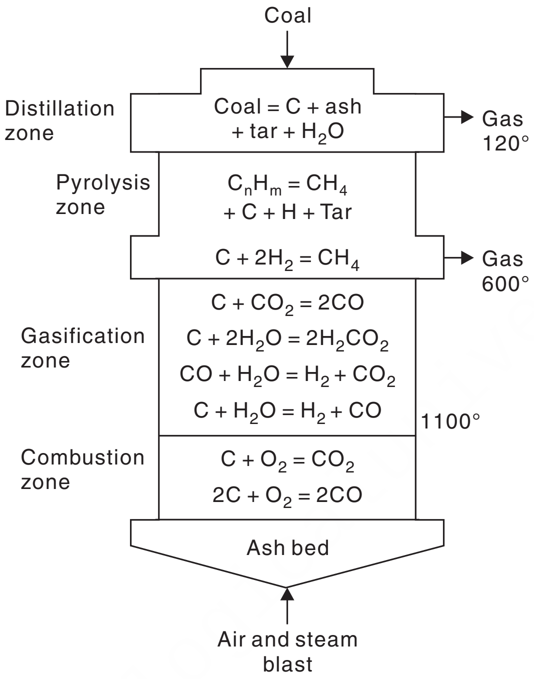


Fig. 18.17 Showing gasification reactions involved in a gasifier.

EXERCISES

1. What is sweetening of petrol?
2. What is flue gas? How is it analysed?
3. Describe the fluidized bed cracking of petroleum mentioning the catalysts used.
4. Describe the manufacture of producer gas? What are its uses?
5. What is leaded-petrol?
6. Write the difference between proximate and ultimate analyses.
7. Describe the manufacture of biogas from waste materials.
8. How is the calorific value of a fuel determined?
9. Write notes on:
    (*i*) Bomb calorimeter.
    (*ii*) Octane number
    (*iii*) Catalytic cracking
    (*iv*) Proximate analysis.
10. What is carbonization? Write the advantages of high temperature carbonization.
11. What is power alcohol?
12. Write a brief note on:
    (*i*) Synthetic petrol
    (*ii*) Blue water gas.

13. (*a*) What are fuels? How do you classify them? Describe methods employed for ultimate analysis of coal.

(*b*) Explain the terms (*i*) Knocking (*ii*) Octane number (*iii*) Cetane number.

14. (*a*) What is sweetening of petrol? Name the various fractions obtained during the fractional distillation of crude petroleum oil.

(*b*) What is the flue gas? How is it analysed?

15. What is meant by cracking of petroleum? Describe various methods used for cracking of petroleum.

16. Write a short note on biogas.

17. Describe fixed bed catalytic cracking.

18. How are gross and net calorific values of a solid fuel determined using a Bomb calorimeter?

19. Give a detailed account of petroleum refining.

20. Give at least four advantages of catalytic cracking over thermal cracking.

21. What is L.P.G.? Give its uses.

22. What do you understand by cetane number of a fuel? Distinguish between high speed diesel and low speed diesel.

23. Mention advantages and disadvantages of a gaseous fuel.

24. What is the difference between claking coals and coking coals?

25. What is power alcohol? Mention its merits and demerits?

26. Give the constituents and uses of Gobar gas.

27. Discuss giving equations, sketch, manufacture and composition of:

(*a*) Producer gas (*b*) Water gas (*c*) Oil gas.

28. Write a short note on:

Orsat’s method of flue gas analysis and its significance.

29. Write short notes on:

(*i*) Catalytic converter (*ii*) Octane and cetane numbers.

30. Write a short note on: Carburetted water gas.

31. What is ultimate analysis of coal?

32. What is the difference between H.T.C. and L.T.C.?

33. Mention the byproducts of coking of coal.

OBJECTIVE TYPE QUESTIONS

1. Which of the fuel gases has highest calorific value?

(*a*) Water gas (*b*) Coal gas (*c*) Producer gas.

2. The calorific value of a coal sample is higher if its

(*a*) Moisture content is high

(*b*) Volatile matter is high

(*c*) Fixed carbon is high.

3. Calorific value of coal is decreased due to presence of

(*a*) Carbon (*b*) Sulfur (*c*) Hydrogen (*d*) Oxygen.

4. Which of the following contains highest percentage of volatile matter?

(*a*) Peat (*b*) Lignite (*c*) Bituminous coal (*d*) Anthracite.

5. Analysis of flue gases is done by:
(*a*) Bomb calorimeter (*b*) Orsat's apparatus (*c*) Boy's gas calorimeter.

6. Alcohol-blended petrol possesses
(*a*) Better calorific value
(*b*) Reduced antiknock properties
(*c*) Better antiknock properties.

7. Anthracite is a coal of
(*a*) Highest calorific value
(*b*) Lowest rank
(*c*) High volatile matter.

8. Fuel gas used as a source of hydrogen is
(*a*) Natural gas (*b*) Producer gas (*c*) Water gas.

9. Isooctane has an octane rating of
(*a*) Zero (*b*) 100 (*c*) More than 100.

10. Better diesel fuel is determined by
(*a*) Octane rating (*b*) Cetane number (*c*) C content.

11. Producer gas is a mixture of
(*a*) $CO + H_2$ (*b*) $CH_4 + H_2$ (*c*) $CO + N_2$

12. Fuel for jet plane is
(*a*) Aviation gasoline (*b*) Kerosene (*c*) Diesel.

13. Natural gas is composed of:
(*a*) *n*-butane (*b*) Methane (*c*) Isooctane.

14. Proximate analysis of fuel determines the percentage of
(*a*) C, H_2O, ash and volatile matter
(*b*) C, H, N, S (*c*) C and H.

15. Bomb calorimeter is used to measure
(*a*) Calorific value (*b*) Carbon content (*c*) Knocking properties.

19

Silicate Technology

INTRODUCTION

Glass and Pottery are the earliest products of man made chemical industry. Glass was known to the ancient Egyptians 6000 years ago. Glass is an amorphous, transparent or translucent, rigid super supercooled liquid of infinitely high viscosity comprising of *metallic silicates* one of which is usually of an alkali metal. Ceramic products are made of clay which are silicates, cement is also a mixture of silicates and other compounds. So, all these industries fall under silicate technology.

Silicates are chemical compounds of silicon and oxygen with metals. Clay and soil are different products. Clay must not be confused with soil. Soil is the thin outermost layer of the earth. *Soil is infact a mixture of clay, sand, humus (decayed vegetable matter) and various other minerals.*

Clay is a mixture of variety of minerals like bentonite, kaolinite, hauoysite etc. Basically most of these are *hydrated silicates of aluminium.* The structural pattern of silicates are important in different ceramic products which have been shown in following figures: In a silicate unit silicon atom is symmetrically surrounded by four oxygen atoms to form a tetrahedral unit. These tetrahedral units remain joined in the silicates (see Fig. 19.1).

Chain silicates. These silicates are of two types *viz., single chain silicates and double chain silicates.* Single chain silicates contain $[(SiO_3)_n]^{-2n}$ ion as the primary unit (Fig. 19.1), while double chain silicates contain $[(Si_4O_{11})_n]^{-6n}$ as the primary unit (Fig. 19.2).

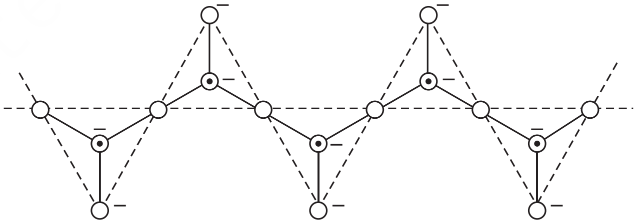


Fig. 19.1 Structure of $[(SiO_3)_n]^{-2n}$ ion (single chain). ⊙ — Silicon atom, ○ — Oxygen atom.

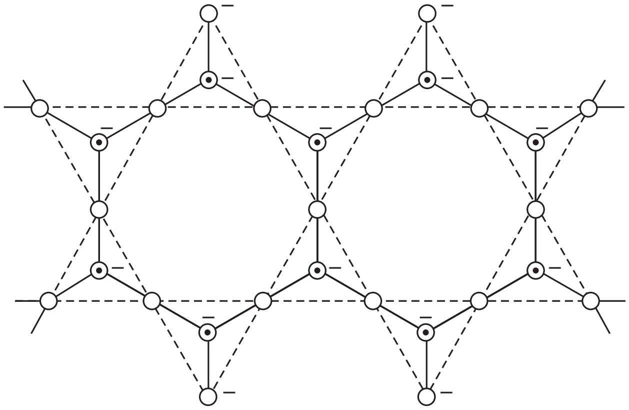
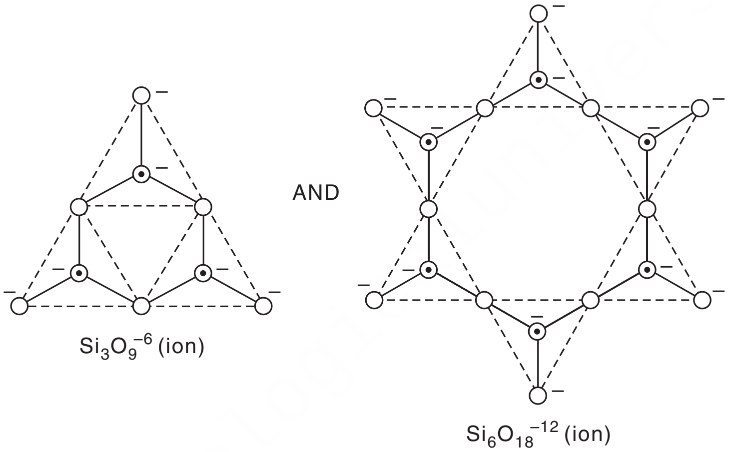


Fig. 19.2 Structure of $[(Si_4O_{11})_n]^{6n-}$ ion (double chain).

It may be noted that O-atoms, which are shared by SiO_4^{4-} tetrahedrons, do not contain any negative charge, *i.e.,* O-atoms, forming a bridge between SiO_4^{4-} tetrahedral units, do not carry any negative charge, O-atoms, forming no bridge, carry negative charge.

Cyclic or ring silicates (Fig. 19.3). These silicates have cyclic structure and contain $[(SiO_3)_n]^{-2n}$ ion as the primary unit. These silicates are formed when each SiO_4^{4-} tetrahedron shares two O-atoms (bridging O-atoms). *Bentonite* is an example: $BaTiSi_3O_9$.



$Si_3O_9^{-6}$ (ion)

$Si_6O_{18}^{-12}$ (ion)

Fig. 19.3 Structure of $Si_3O_9^{-6}$ and $Si_6O_{18}^{-12}$ ions (ring).

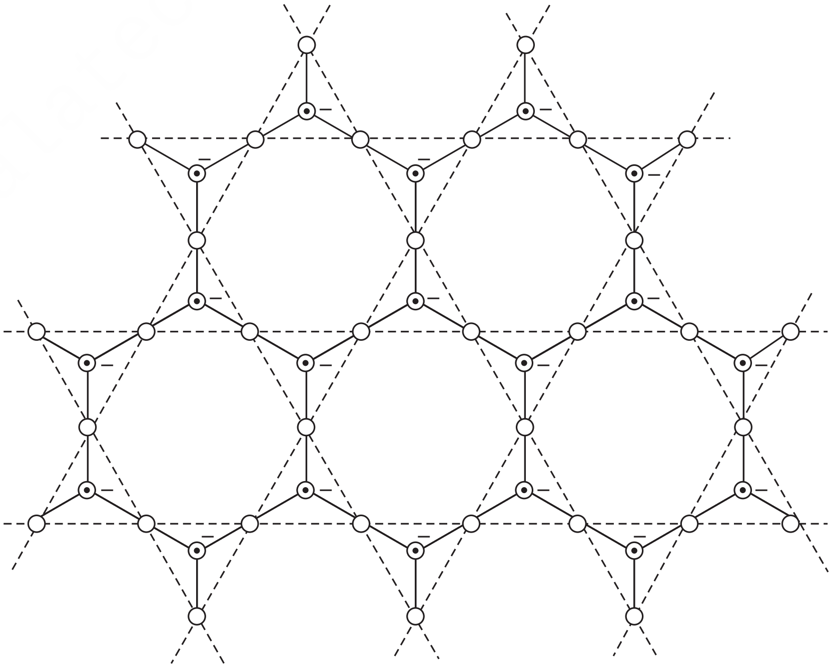


Fig. 19.4 Structure of sheet silicates (layered structure).

Clay or silicates are common raw materials for

- Ceramic industries
- Refractory industries
- Glass industries and
- Cement industries.

For that reason the technologies of these industries fall under the common name *silicate technology*. Generally silicate materials are bad conductor of heat and electricity. Now-a-days, some new types of ceramics are discovered with electrical and magnetic properties. These properties depend on their unit structure. These ceramics are called *high performance ceramics*. The individual solid metal oxides were mixed in the proper ratio, ground well and finally heated to 1000°C for 12 hrs, at this high temperature the individual oxides are converted into the mixed oxide compound. The property of super-conductivity in these compounds is dependent on a particular characteristic of arrangements of constituent atoms. For example, in $YBa_2Cu_3O_{7-y}$ (see Fig. 19.5) successive horizontal layers of copper-oxygen sheets are separated by ribbon-like chains of copper-oxygen. The square copper-oxygen sheets are the pathways of super-conducting electrons in these compounds. Even slight alteration of the arrangement of atoms destroys superconductivity. The preparation of superconducting ceramic therefore, is an exacting piece of work.

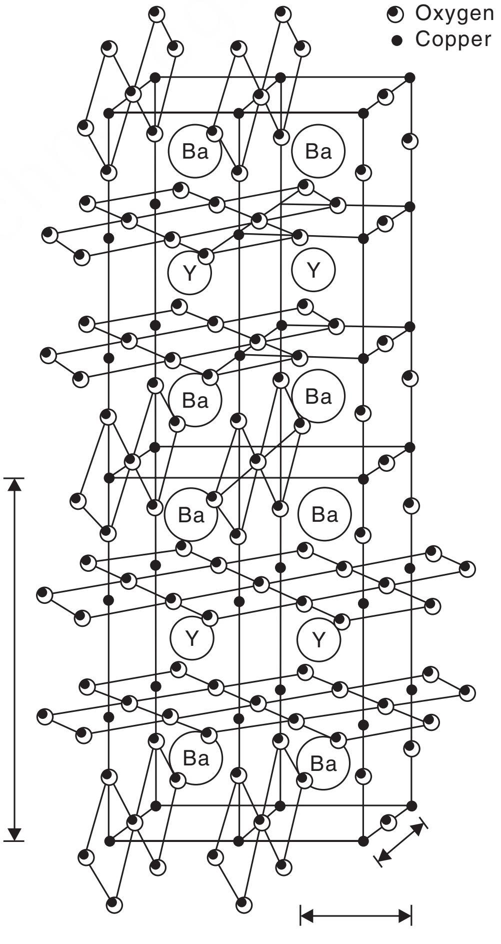


Fig. 19.5 The crystal lattice of $YBa_2Cu_3O_{7-y}$.

These types of superconductors are used in superfast magnetically leviated (maglev) train *i.e.*, superfast floating train. This is an example of application ceramic superconductor like $YBa_2Cu_3O_{7-y}$.

CEMENT

The present day civilization very much depends upon lime, mortar and cement products, *viz.* reinforced-concrete walls and girders (a chief beam), tunnels, dams and roads etc. The tremendous application of these products is due to their:

- Convenience
- Cheapness
- Adaptability
- Strength
- Durability

Man had early discovered certain natural rocks. The rocks on calcination gave a product that hardened on the addition of water. Cement was first used by the Egyptians in constructing the pyramids. The Greek and Romans used volcanic tuff for cement and a number of these structures are still standing. In 1824, an Englishman, Joseph Aspdin, patented an artificial cement made by the calcination of an argillaceous lime stone (argil-clay). He called this 'Portland' as concrete made from it resembled a famous building stone obtained from the Portland island near England. This was the start of the Portland cement industry as we know it today. The hard clinkers (Brick type) resulting from the burning of argilaceous limestone is known by the term *Portland cement* to distinguish it from natural or Pozzuolana and other cements.

The cement will set under water and therefore it is known by the name of *Hydraulic cement*. A cement is a substance, which sets to a hard mass in presence of water. Two types of cements are in use.

- Roman cement
- Portland cement.

Of these, Portland cement is now manufactured on a large scale. *Portland cement is made by mixing calcareous (lime-stone) and argilaceous materials in the proper ratios and heating to the point of incipient fusion in a kiln and grinding the resulting clinker.* The raw materials should be so proportioned as to produce a cement in which the ratio of the amount of CaO to the amount of ($2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3$) should not be more than 1.02 and not less than 0.66 *i.e.*,

$$0.66 \le \frac{CaO}{2.8\,SiO_2 + 1.2\,Al_2O_3 + 0.65\,Fe_2O_3} \le 1.02$$

The Portland cement is a mixture of the following compounds:

Compounds	*Formula*	*Abbreviation*
(*i*) Tricalcium aluminate	$3\ CaO\ .\ Al_2O_3$ **or** $(CaO)_3\ .\ Al_2O_3$	C_3A
(*ii*) Tricalcium silicate	$3\ CaO\ .\ SiO_2$ **or** $(CaO)_3\ .\ SiO_2$	C_3S
(*iii*) Dicalcium silicate	$(CaO_2)\ .\ SiO_2$ **or** $2CaO\ .\ SiO_2$	C_2S
(*iv*) Tetracalcium alumino ferrate	$(CaO)_4Al_2O_3\ .\ Fe_2O_3$ **or** $4CaO\ .\ Al_2O_3\ .\ Fe_2O_3$	C_4AF

Small amount of MgO derived from the raw materials is also present. Some cement contains gypsum or plaster of paris, which is added in small quantities to increase the plasticity of cement.

Varieties of Cement

- *Portland cement.* The regular Portland cement contains medium amount of CaO. *White cement contains less ferric oxide.* High early strength cement [H.E.S] is made from a raw material with a high lime to silica ratio. It contains a higher proportion of C_3S than regular Portland cement and hence hardens much more quickly. Roads constructed from H.E.S. can be put into service more quickly than if regular cement had been employed. Low heat portland cement contains high proportion of C_4AF and C_2S. A concrete of better chemical resistance contains high proportion of C_4AF.
- *Pozzuolana cement.* A pozzuolana is a material, which is not cementitious in itself but becomes so upon mixing with lime. The natural pozzuolana are volcanic tuffs, the artificial ones are burnt clays and shales.
- *High alumina cement.* It is manufactured by fusing a mixture of limestone and bauxite (contains Fe_2O_3, SiO_2, MgO etc). It is characterised by a very rapid rate of development of strength and superior resistance to sea water and sulphate carrying water.
- *Special or corrosion resisting cement.* It is mainly used for the fabrication of corrosion proof linings for chemical equipment such as storage tanks, absorption towers, acid digesters etc. Example: phenolic cement–phenol formaldehyde resins.

Raw Materials

Formerly a large proportion of cement was burned from argilaceous limestone known as cement rock. In industries for CaO of cement, chalk, cement rock and marl (mixture of $CaCO_3$) and clay are used. In addition to natural materials some plants use artificial products such as blast furnace slag and precipitated $CaCO_3$ obtained as a by-product in alkali and synthetic ammonium sulphate industry.

Sand, waste bauxite and iron ore are sometimes consumed in small amounts to adjust the composition of the mix. Gypsum (2-3%) is added to prevent rapid setting of the C_3A.

List of Raw Materials: Limestone, cement rock, clay and shale, gypsum, blast furnace slag, sand, sandstone, marl, iron material, precipitated calcium carbonate and misc.

In India, the byproduct precipitated $CaCO_3$ from Sindri Fertilizer Corporation of India was utilised by A.C.C. Bihar company to manufacture cement. Rohtas Industries Ltd., Dalmianagar, Delhi uses (1) Laterite (red clay) and (2) limestone. Limestone is partly replaced by the $CaCO_3$ mud obtained as by-product during clarification of sugarcane juice at the sugar factory of the same company.

A processing of available raw materials is necessary to correct the proportions of the mineral sources of the four oxides of Ca, Si, Al and Fe essential for cement manufacturing and discard useless constituents, *i.e.,* the purpose is to '*benificiate*' available raw materials and hence the process is named *beneficiation* process. This may involve the raising of the lime content of the raw materials or it may be for the elimination of the greater part of the silica as compared to the alumina. The complete process involves a combination of **(1) grinding, (2) classification, (3) floatation and (4) thickening operation**.

In making these differential separations, very small quantities of collecting reagents are employed. The collecting agent must selectively wet or 'film' the mineral to be removed and act with the air to cause the particles to be lifted to the surface making a froth. That is, the froth floatation process is used to remove the undesirable material in the froth and oleic acid may be employed as the *collector*. A concentration of 0.04 lb per ton of rock suspended in 4 tons of water has given good results. Frothing aids in separation of desired materials from the undesired ones.

Manufacturing Procedure

Two methods of manufacture are used:

- ***Wet process***
- ***Dry process***

The wet process was the original one. For a time it was gradually displaced by the dry process. But the wet process is now being adopted largely for new plants for more accurate control and mixing of the raw mixture.

In the wet process, the solid material after dry crushing is reduced to a fine state of division in wet tube or ball mills and passes as a slurry through the bowl classifiers or screens. The slurry is pumped to correcting tanks where rotating arms make the mixture homogeneous and allow the final adjustment in composition of raw materials to be made. This slurry is filtered in a continuous rotary filter and fed into the kiln. The moisture content of the feed is 40%.

The dry process is especially applicable to natural cement rock and to the mixtures of limestone and shale or slate. In this process, the materials are roughly crushed in jaw crushers followed by gyratory mills, then dried, sized and more finely ground in tube mills. This dry powdered material (moisture content 2%) is fed directly to the kiln. Heat is provided by burning oil, gas or pulverised coal, using preheated air from cooling the clinker. 80-160 lbs of fuel are necessary per barrel (376 lbs) of cement.

The tendency in recent years has been to lengthen the rotary kiln in order to increase its thermal efficiency. Dry process kilns may be as short as 150 ft, but in the wet process, 300-500 ft kilns are not uncommon. The internal diameter is usually 8 to 15 ft. The kilns are rotated at from 1/2 to 2 r.p.m., depending on size. The kilns are slightly inclined so that materials fed in at the upper end and travel slowly to the lower end, taking from 2-3 hrs (Fig. 19.6).

In order to obtain greater heat economy, unit operations are used for removing the part of the water from slurry by slurry filters. Waste heat boilers are used to conserve heat.

Because the lining of kiln has to withstand severe abrasion and chemical attack at the high temperatures in the clinkering zone, the choice of refractory linning is difficult. For this reason, high alumina bricks and high magnesia bricks are widely used for the lining of the kiln, although Portland cement clinker itself is satisfactory for the purpose.

Reactions at various temperatures in the kiln

Temperature	*Reactions*	*Heat change*
100°C	Evaporation of water ($H_2O\uparrow$)	Endothermic
> 500°C	$Al_2O_3 . SiO_2 . xH_2O \longrightarrow Al_2O_3.SiO_2 + xH_2O$	Endothermic
> 900°C	$CaCO_3 \longrightarrow CaO + CO_2\uparrow$	Endothermic
900°C to 1200°C	*$5CaO + 3 Al_2O_3 \longrightarrow 5 CaO . 3Al_2O_3$ $2CaO + SiO_2 \longrightarrow 2CaO . SiO_2$	
	$3CaO + SiO_2 \longrightarrow 2CaO . SiO_2$	Exothermic
	$2CaO + Al_2O_3 \longrightarrow 2CaO . Al_2O_3$	
	$3CaO + Al_2O_3 \longrightarrow 3CaO . Al_2O_3$	

(*Contd...*)

1250°C – 1280°C > 1280°C	Commencement of liquid formation Further formation of liquid and compounds	Endothermic Endothermic
	*Main reactions between lime and clay. Lime produced combines with main constituents of clay *viz.* Al_2O_3 and SiO_2.	

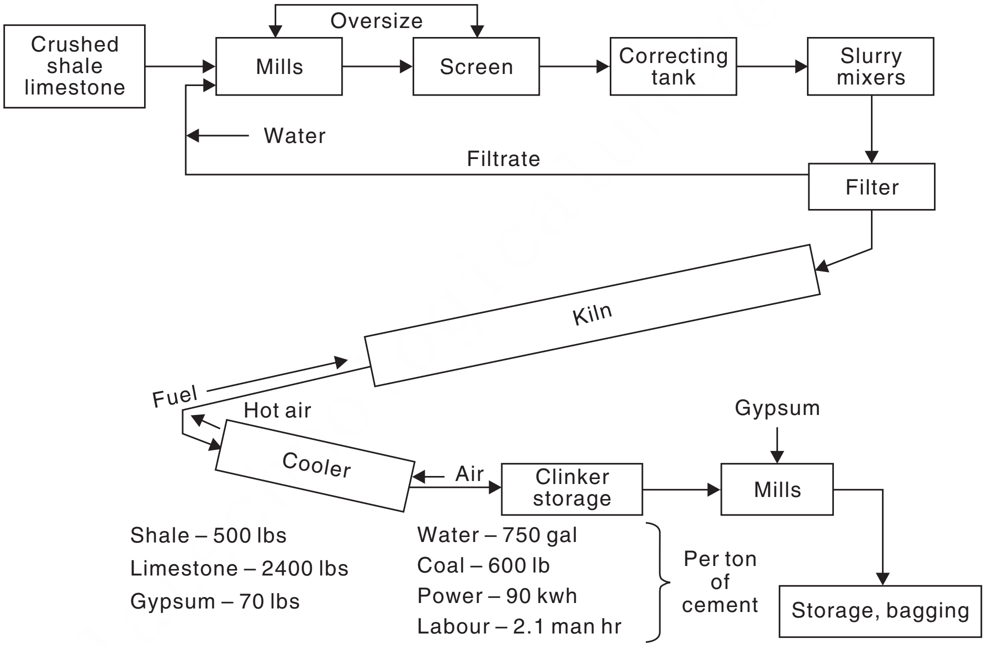


Fig. 19.6 Wet process for cement manufacture.

The analysis of typical samples of cement gives the following composition:

Lime ⇒ 55.06%; SiO_2 ⇒ 22.92%; Al_2O_3 ⇒ 8%
Fe_2O_3 ⇒ 5.46%; MgO ⇒ 0.77%; Potash ⇒ 1.13%
Soda ⇒ 1.7%; $CaSO_4$ ⇒ 1.75%; Unchanged clay and sand ⇒ 2.27%.

The final product formed consists of hard grannular masses from 1/8 to 3/4 inches in size, called **clinker**. The clinker falls through openings in the stationary firing ring of the kiln into rotating coolers, which simultaneously preheat the combustion air. Pulverising followed by the fine grinding in tube ball mills and packaging complete the steps to the finished cement. During fine grinding the following materials are added to the finished cement.

- Retarders such as gypsum
- Plaster or calcium lignosulphate
- Air entraining agents
- Dispersing agents and
- Waterproofing agents

Setting or Hardening of Cement

Setting of cement is a complicated process, and the cause of setting has been the subject of much discussion. But it is generally agreed that this takes place by hydration and hydrolysis.

On addition of water, the calcium compounds are decomposed with the formation of free $Ca(OH)_2$ and hydrated crystalline silicate and calcium aluminate, the crystals of which form an interlaced mass. Due to this interlacing of crystals the setting of cement occurs. The following equations represent these reactions:

$$C_2S + xH_2O \longrightarrow C_2S \,.\, xH_2O \text{ (amorphous)}$$
$$C_3S + xH_2O \longrightarrow C_2S \,.\, (x-1)\, H_2O \text{ (amorphous)} + Ca(OH)_2$$
$$C_3A + 6H_2O \longrightarrow C_3A \,.\, 6H_2O(c)$$

The hydration products have very low solubility in water. If this was not true, concrete would have been rapidly attacked in contact with water.

Another theory suggests that due to hydration, cement is converted into a gel of composition $C_3A.\ 6H_2O$ with absorbed water. This is followed by a slow crystallisation of the gel. The rapid increase in strength and hardness during setting of cement is mainly due to the partial hydrolysis of C_3S to form needles of $Ca(OH)_2$ in the hydrated silicate gel.

To hold up the 'flash set' caused by C_3A, some investigators assert that the gypsum added as retarder causes the temporary formation of $C_3A.3CaSO_4.3H_2O$, while others believe that the gypsum gives free $Ca(OH)_2$ by reaction with alkali and this in turn forms the more stable $C_4A(4CaO.Al_2O_3)$. The following equations represent these reactions:

$$C_3A + 6H_2O \longrightarrow C_3A \,.\, 6H_2O(c)$$
$$C_3A + 3(CaSO_4 \,.\, 2H_2O) + 25\, H_2O \longrightarrow C_3A \,.\, 3CaSO_4 \,.\, 31H_2O$$
$$C_4AF + xH_2O \longrightarrow C_3A \,.\, 6H_2O(c) + CaO \,.\, Fe_2O_3 \,.\, (x-6)\, H_2O$$
$$MgO + H_2O \longrightarrow Mg(OH)_2$$

The various compounds contribute to the heat of setting as follows:

$$C_3A > C_3S > C_4AF > C_2S$$

Lower heat of setting of cements are made low in C_3A and C_3S but high in C_2S by adding more Fe_2O_3, which takes the Al_2O_3 as C_4AF, thereby diminishing the amount of C_3A and by decreasing the CaO/SiO_2 ratio. This low heat of setting cement is used for construction of dams to avoid cracking the structure from heat stresses during setting and cooling. As an additional safeguard, the structure may be cooled during setting by circulating cold water.

The following table displays the functions of various compounds of cement.

Compounds	*Function*
C_3A	Responsible for initial set (flash set)
C_3S	Responsible for 1st strength (after 8 days)
C_2S and C_3S	Responsible for final strength (at 1 yr).
Fe_2O_3, Al_2O_3, Mg and alkalies	Lower clinkering temperature

GLASS

Glasses are *Ceramic materials* that are rigid like solids but which are not crystalline. *Glass may be considered as supercooled liquid of infinitely high viscosity.* Glass is made by melting one or more oxides in a furnace. The liquid glass is cooled until thick enough to mould and then shaped and cooled further slowly (annealing) until it sets to a solid mass.

Most glass is made from silica mixed with other oxides that melt at a lower temperature than glass made from pure silica; windows, bottles, and drinking water glasses are made of soda lime glass. Lead glass is used for decorative cut glassware. *Borosilicate glass* is used to make ovenware and laboratory glassware.

Compostion of glass

Glass is not a single compound. It is difficult to write any chemical formula for it. Generally the formula for glass may be represented thus,

$$xR_2O.\ yMO.\ 6SiO_2$$

where R = alkali metal (Na, K etc.)

M = bivalent metal (Ca, Pb etc.)

x and y = number of molecules.

Different varieties of glass

- *Vitreous Silica (quartz glass).* A glass made by fusing pure silica without a flux and is very resistant thermally and chemically. Used beyond the temperature ranges of other glasses. Transparent to U.V. radiation (ordinary glass is not transparent to U.V.).
- *Alkali silicates [Soluble glass (Soda), soluble glass (Potash), Water glass* ($Na_2O\ .\ SiO_2$. $K_2O\ .\ SiO_2$)] used in soap manufacture, for preservation of eggs, in the manufacture of artificial stones.
- *Lime glass*

(*a*) Soda lime glass, soda glass, soft glass ($Na_2O.CaO.6SiO_2$) are easily fusible, low softening temperature.

Uses. Laboratory apparatus, window and plate glass.

(*b*) Potash lime glass [Bohemian glass, Hard glass] ($K_2O.CaO.6SiO_2$). Fusion temperatures high.

Uses. Chemical apparatus withstanding high temperatures, specially combustion tubes.

- *Lead glass [Potash lead glass, Flint glass]*

($K_2O.PbO.6SiO_2$) fuses easily. sp. gr. higher; refractive index, μ = 1.7-1.78 (higher than that of common glass, μ = 1.5)

Uses.

(*a*) decoration and optical effects

(*b*) manufacture of lens and prism

(*c*) artificial gems

(*d*) electric bulbs.

- *Borosilicate glass.* When part of SiO_2 in glass formulation is replaced by B_2O_3 the glass formula becomes $7Na_2O.4CaO$, $3ZnO.36(SiO_2 + B_2O_3)$; usually contains B_2O_3 = 10-13%, SiO_2 = 80-83%, low expansion coefficients, superior resistance to shock, excellent chemical stability, high electrical resistance.

Uses. Wide and ever increasing uses for these properties for laboratory glassware.

Special glasses

1. Coloured glasses

- Colour is produced by the absorption of certain light frequencies by agents in solution in the glass. The colouring agents of this group are the oxides of transitional elements, especially the first group: Ti, V, Cr, Mn, Fe, Co, Ni and Cu.

- Colour is produced by colloidal particles precipitated within an originally colourless glass by heat treatment.

Example is the precipitation of gold (colloidal) producing gold ruby glass.

- Colour is produced by microscopic or larger practicles. Selenium rods (SeO_2) used in traffic lights.

2. Opal, translucent or ground glass (ghosa kanch)

Soft glass made translucent by rubbing the surface with emery powder and turpentine, or sand and water, using HF.

3. Safety or laminated glass

Two layers of glass with an interleaf of plastic. When the glass is broken the fragments are held in place by inter layer.

4. Fibre glass

- Glass wool is impregnated with various binders and used for insulation.
- It can be spun into yarn.

5. Phosphate glass

It contains P_2O_5 as a major ingredient, wholly or partially displacing SiO_2. It can resist HF. Sight glasses for the handling of uranium hexafluoride in separation of uranium isotopes are made of phosphate glass.

6. High silica glass

96% SiO_2, 3% B_2O_3 and the rest Al_2O_3. This glass has high chemical durability and is extremely stable to all acids except HF, which attacks more slowly than others.

Properties of glass

- Physical:

(*a*) Transparent (usually) amorphous solid,

(*b*) Vitrifies easily, but devitrifies by formation of crystals under suitable conditions. On long standing or very slow cooling during annealing some of metallic silicates crystallise out. Glass is then said to devitrify.

(*c*) Hard and brittle

(*d*) No fixed melting point

(*e*) Bad conductor of heat and electricity

(*f*) Can incorporate colour maintaining transparency

- Chemical:

(*a*) Not attacked by air, water, oxidising agents, acids. Only attacked by HF readily.

$$Na_2O \,.\, SiO_2 + 6HF \longrightarrow 2NaF + SiF_4 + 3H_2O$$
$$CaO \,.\, SiO_2 + 6HF \longrightarrow CaF_2 + SiF_4 + 3H_2O$$

(*b*) Ordinary glass attacked by alkali solutions.

Functions of different constituents of glass

(*a*) K_2O: increases the softening point.

(*b*) Fe_2O_3: Inability to transmit UV is due to the presence of FeO or Fe_2O_3 in glass. Using iron free raw materials, glass capable of transmitting UV light could be manufactured.

(*c*) PbO: increases the refractive index of glass.

(*d*) B_2O_3: increases the hardness or refractory characters of glass and lowers expansion coefficient.

Raw materials

The raw materials employed in the manufacture of glass can be classified under three heads:

1. Substances of an acid character, like SiO_2, B_2O_3.
2. Substances of basic character, like soda, potash, lime, MgO, BaO, ZnO, PbO etc.
3. Various decolourising and opacifying agents like MnO_2, Pb_3O_4, nitre, Zn-compounds, SnO_2 etc.

Certain colour producing oxides are used for producing coloured glass, *e.g.,* CuO for blue colour, Cu_2O for ruby or red colour, Cr_2O_3, Fe_3O_4 for green colour, MnO_2 for violet colour etc.

- Silica is used in the form of sand. It is almost pure quartz (white sand) of which iron content should not exceed 0.045%.
- Soda, Na_2O is principally supplied by soda ash, Na_2CO_3. Other sources are salt cake and $NaNO_3$. The latter is useful in oxidising iron and accelerating the melting.
- The important sources for lime, (CaO) are limestone and burnt lime from dolomite, $CaCO_3$, $MgCO_3$. The latter introducing MgO into the batch.
- Potash is always used in the form of K_2CO_3.
- ZnO is sometimes used to replace lime.
- BaO as such or as precipitated $BaCO_3$.
- PbO in the form of Pb_3O_4.
- Boric acid as such or as B_2O_3.
- H_3PO_4 is used as an opacifying agent.
- Feldspars having the general formula $R_2O.Al_2O_3.6SiO_2$. Feldspars supply Na_2O or $K_2O.(R_2O)$ and $SiO_2.Al_2O_3$ serves to lower the melting point of the glass and to retard *devitrification.* Devitrification means slow crystallisation.
- *Cullet* is crushed glass from imperfect articles. It facilitates melting and utilises waste. It may be as low as 10% of the charge or as high as 80% of the charge.

Chemical reactions of the formation of glass in a furnace

$$Na_2CO_3 + a\,SiO_2 \longrightarrow Na_2O\,.\,a\,SiO_2 + CO_2$$

$$CaCO_3 + b\,SiO_2 \longrightarrow CaO\,.\,b\,SiO_2 + CO_2$$

$$Na_2SO_4 + c\,SiO_2 + C \longrightarrow Na_2O\,.\,c\,SiO_2 + SO_2 + CO.$$

- It should be noted that the ratios Na_2O/SiO_2 and CaO/SiO_2 need not be 1:1 molecular ratios.
- The compounds may be of the type $Na_2O.1.8SiO_2$.
- In window glass molecular ratios are approximately $2Na_2O.CaO.5SiO_2$.
- For decolourisation, MnO_2 is added to the charges which oxidises Fe^{+2} to Fe^{+3}. The green colour due to ferrous silicate being changed to yellow colour due to ferric silicate.

This yellow colour is rectified by the pale violet colour due to manganese silicate and a perfect white glass results.

Manufacturing procedure

The manufacturing procedure is divided into four major phases:

(*i*) Melting
(*ii*) Shaping
(*iii*) Annealing
(*iv*) Finishing

(*i*) **Melting.** Two types of furnaces are in use:

(*a*) *Pot furnaces* (*b*) *Tank furnaces*

Pot furnaces are employed principally in the manufacture of optical glass, art glass and plate glass and in the small scale units. The pots are really crucibles made of selected clay, high alumina fire clay such as *mulite* ($3Al_2O_3 . 2SiO_2$) or platinum. The material of the pot is attacked by prolonged action of molten glass and hence has to be changed after a number of operations except when platinum is used.

In a tank furnace, batch materials are charged into one end of a large 'tank' built of refractory blocks. The tank measures 125′ × 30′ × 5′ with a capacity of 1400 tons. The glass forms a pool in the hearth of the furnace across which the flames play alternately from one side to the other.

The 'formed' glass is worked out of the opposite end of the tank. The operation is continuous. The walls of tank furnace gradually wear away under the action hot glass.

The furnaces may be of either regenerative or recuperative design. In either of the cases the heat from the hot gases is utilised in preheating the air, for combustion of the fuel. Once the furnace has been heated, a temperature 1205°C is maintained all the time. The larger part of the heat is lost by radiation from the furnace walls.

This sort of heat loss is necessary to reduce the action of the molten glass on the furnace wall. Otherwise the furnace wall will corrode. Sometimes water cooling pipes are used to cool the furnace wall.

(*ii*) **Shaping or forming.** The glass articles are shaped either manually or by machine. In order to produce a sheet glass first a cylinder of approximate size is blown into shape. It is allowed to stand vertically on a stand. The cylinder is cut open by running a sharp knife lengthwise. At present every stage of shaping has been mechanised. The blowing is done by compressed air.

(*iii*) **Annealing.** To reduce strains, it is necessary to anneal all glass objects. Annealing involves two operations:

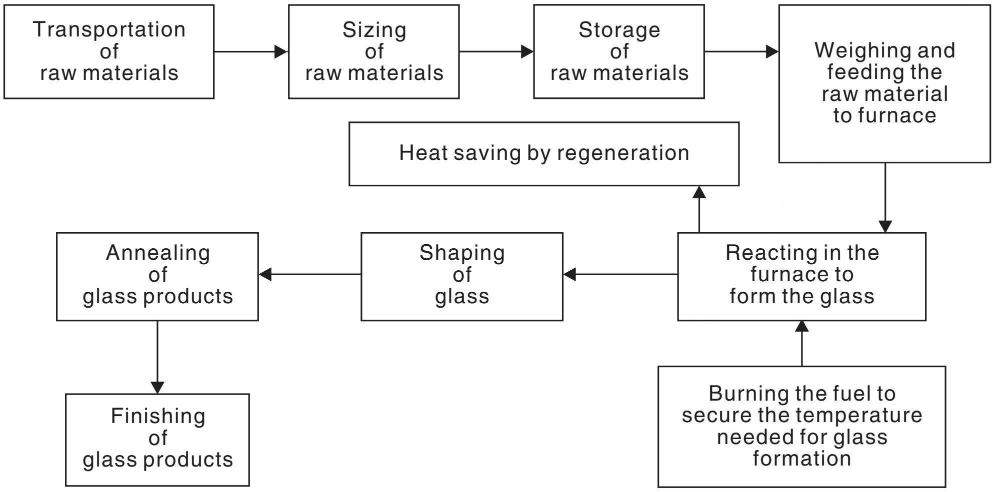
(*i*) Holding a mass of glass above a certain critical temperature, long enough to reduce internal strain by plastic flow.
(*ii*) Cooling the mass to room temperature slowly.

The annealing oven is nothing more than a carefully designed heated chamber in which the rate of cooling can be controlled.

(*iv*) **Finishing.** All types of glass articles must undergo certain finishing operations.

These include cleaning, grinding, polishing, cutting, enameling etc. Although all these are not required for every glass object, one or more is almost always necessary.

Flow diagram mentioning manufacturing sequences for glass



POTTERY AND PORCELAIN

They are generally clay fired products, sometimes enamelled or glazed.

Clay

Geologically, clays are regarded as the products of disintegration and weathering of granite rocks, in which feldspar was a original mineral but the term is also applied to most minerals which possess the property of being plastic when mixed with a suitable amount of water.

Weathering reaction:

$$\underset{\text{feldspar}}{K_2O \cdot Al_2O_3 \cdot 6SiO_2} + CO_2 + 2H_2O \longrightarrow K_2CO_3 + \underset{\text{kaolinite}}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} + 4SiO_2$$

Common clay

It is principally aluminium silicate mixed up with a large number of substances *viz*, compounds of Fe, Mn, Ca, Mg etc. and vegetable matters.

Kaolin or China clay

It is a pure *white burning* clay of low plasticity and is formed by weathering of feldspar.

Composition— $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

Fire clay. It contains a good deal of SiO_2 and very little Fe. When fired, it forms a material of high fusing point (1550°C and upwards). Clays are used in the manufacture of bricks, tiles, porcelain wares, pottery articles, electric insulators, drain pipes and other sanitary goods etc.

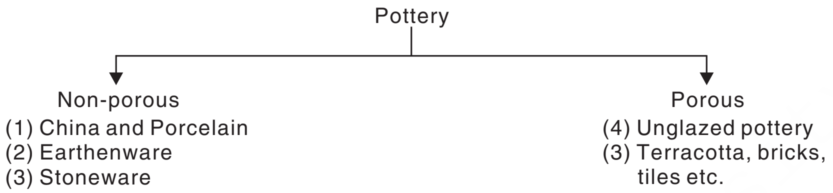
The use of clay in ceramics depends upon its following important properties:

(*i*) It is plastic enough to be moulded when it is wet,

(*ii*) It retains its shape when dried and,

(*iii*) When the moulded mass is heated to a high temperature, it sinters together forming a hard, coherent mass without losing its original colour.

Pottery: (articles made of clay)



Raw materials. The three main raw materials are: (1) clay (kaolinite), (2) feldspar, (3) sand.

Common fluxing agents. Borax, fluorspar, cryolite, boric acid, Na_2CO_3, K_2CO_3, iron oxides.

Common refractory materials. CaO, $CaCO_3$, ZnO_2, TiO_2. Both glazed and unglazed clay products are manufactured. The glazed product is obtained by applying glaze on the unglazed body. For glazing the shaped material is covered with a coating of mixture of powdered feldspar, SiO_2, borax etc., and heated at higher temperature for longer time. The thin coating melts and forms a glaze on the surface of the body. Porcelain, therefore is looked upon as partly glass and partly stoneware.

In all cases, the unglazed product is to be made. The raw materials for unglazed product are:

1. China clay
2. Ball clay
3. Flint (Pure SiO_2 + $CaCO_3$)
4. Cornish stone (Potash feldspar, $K_2O = 6\%$, $CaO = 1\%$, $Al_2O_3 = 18\%$, $SiO_2 = 75\%$)
5. Marble ($CaCO_3$)
6. Quartz (SiO_2).

Raw materials for glaze

Frit. It is a sort of glass. It is made from Borax, Feldspar, Quartz etc.

Stoneware. This is a kind of porcelain. It is not always white because the ingredients contain Fe_2O_3. It is used for sewer pipes. It is glazed with salt.

Chemical stoneware. It is used for making jars suitable for storing acids.

The reactions of porcelain formation are:

$$\underset{\text{China clay}}{3Al_2O_3.2SiO_2.2H_2O} \xrightarrow{600°C} 6H_2O\uparrow + \underset{\text{(amorphous)}}{3Al_2O_3} + \underset{\text{(amorphous)}}{6SiO_2}$$

$$\Big\downarrow 900°C$$

$$\underset{\text{(Crystal)}}{SiO_2} \xleftarrow{1400°C} 4SiO_2 + \underset{\text{Mullite}}{3Al_2O_3.2SiO_2} \xleftarrow[\text{Silicate formation}]{1000°C} \underset{\text{Crystal line}}{\gamma\text{-}3Al_2O_3} + \underset{\text{(amorphous)}}{6SiO_2}$$

Porcelain is used for making– (*i*) dinner and tea sets, (*ii*) basin, crucibles, (*iii*) electrical insulators, floor and wall tiles, (*iv*) high class sanitary goods.

Process: It consists of the following steps:

1. *Slurry preparation:* The mixture of weighed ingredients is taken in a blunger and stirred well with water to form a creamy liquid known as clay slip.
2. *Ageing:* The slip is filter-pressed. The residual cake contains 10-30% water. The cakes are dumped for some days. This improves the plasticity of the clay mixture because of uniform hydration and gelation.
3. *Deairing:* The aged cakes are deaired in a pug mill by slicing with knives and putting under vacuum.
4. *Shaping.*
5. *Trimming and drying:* The shaped articles after airdrying are trimmed and then dried in hot air.
6. *Glazing:* The dried articles known as *blanks* are glazed. In few cases glaze is put on the blanks before firing. But in most cases, blanks are fired to produce biscuits. The firing is done in a tunnel furnace. Usual maximum temperature is 1400°C.

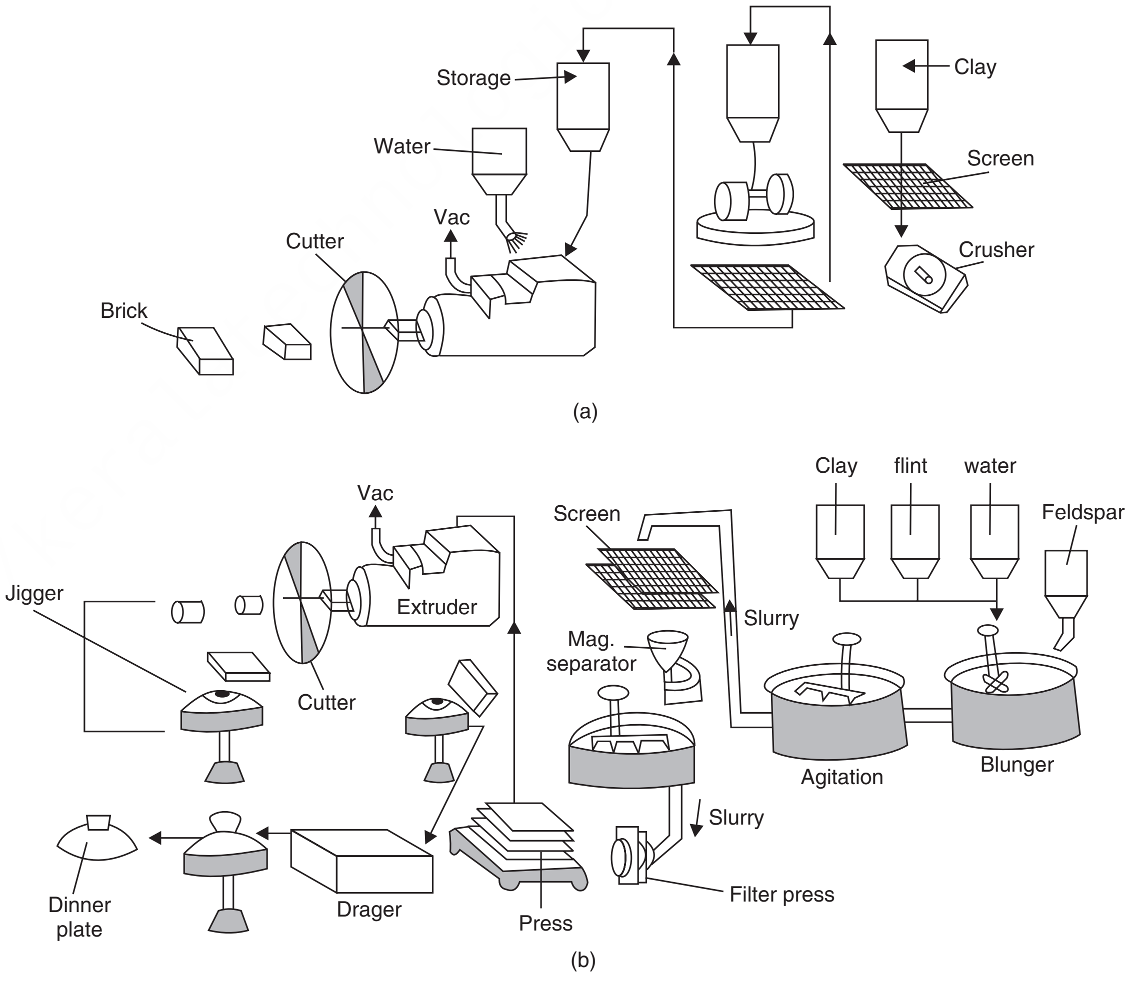


Fig. 19.7 Flow diagram: (*a*) Brick manufacture (*b*) Dinner plate manufacture.

Glazing: The glazing ingredients are finely powdered and mixed. The mixture is mixed with water to make the slip. The slip is next applied to dry blanks or more frequently to the biscuits by dipping or pouring or spraying or brushing very carefully and then heated at 1400°C. Glaze is a sort of glass, which is applied on the surface to cover the pores.

The alkali portion of feldspar and most of the fluxing agents becomes a part of the glassy or vitreous phase of the ceramic body. All ceramic bodies undergo a certain amount of vitrification or glass formation.

REFRACTORIES

The word *refractory* means resistant to melting or fusion. Broadly speaking, refractories are materials which are used to withstand high temperature, chemical and physical effects without softening or suffering a deformation in shape. Whenever very high temperatures are involved as in furnaces, kilns and electrical heating apparatus, the refractories do provide the linings or bricks, supports and other filaments. The main objective of a refractory is to confine heat (*i.e.,* to resist the heat loss) and at the same time to resist the abrasive and corrosive action of molten metals, slags and gases at high operating temperatures. *Thus refractories are those materials which are used for the construction of furnaces, kilns, ovens, crucibles, retorts, converters etc. Refractories are sold in the form of bricks, silica, magnesite, chromite bricks, silicon carbide, and zirconia refractories etc.*

Classification

Refractories are classified broadly under three heads depending on the chemical properties of their constituent substances. These are

(*i*) *Acid refractories:* They are made of clay, clay-silica mixtures and of pure silica. They are not attacked by acidic materials. Examples–silica bricks and fire clay bricks.

(*ii*) *Basic refractories:* They are made up of large proportion of lime or magnesia or a mixture of these bases or other metal oxides.

Examples–Magnesite bricks (magnesia), bauxite bricks.

(*iii*) *Neutral refractories:* They are made up of weakly acidic or basic materials like carbon, chromite (FeO, CrO_2), zirconia (ZrO_2) etc. Examples–Chromite bricks, silicon carbide and graphite.

At present some single oxide bricks have been developed. These are self bonded and have high fusion points. Examples–alumina (2050°C), magnesia (2250°C) and zirconia (2200 °C) etc.

Properties

Refractories should possess the following general properties:

(*i*) They must be able to withstand high temperature.

(*ii*) They should be infusible at the temperature to which they are liable to be exposed. The fusion temperatures of the usual refractories in use vary from 1600°C to 2700°C.

(*iii*) They should be chemically inert towards the corrosive action of gases, liquid metals and slags produced in its immediate contact in furnaces.

(*iv*) They should be able to withstand sudden change of temperature.

(*v*) They should be able to withstand spalling, *i.e.,* cracking and flaking of the bricks due to uniform expansion or contraction. Annealed bricks can better withstand spalling.

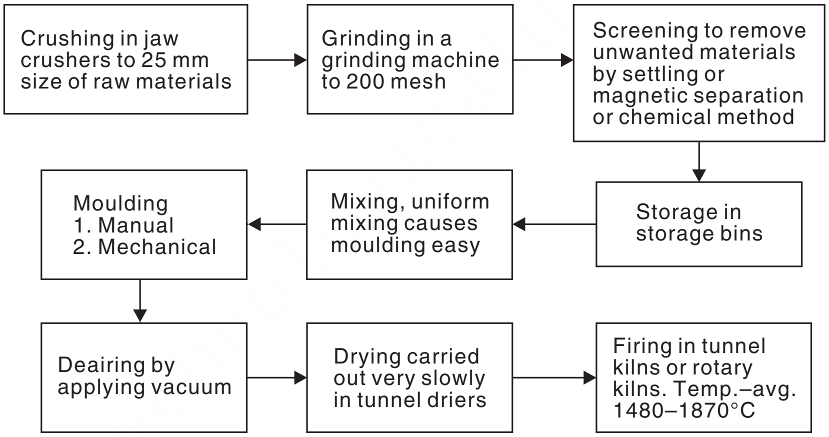
(*vi*) They must be able to withstand abrasion or erosion of the furnace charge and also the pressure of the load.

(*vii*) Porosity of a refractory is a deciding factor of the degree of penetration by molten fluxes and gases and thus the refractory material easily disintegrates, *i.e.,* the greater the porosity, the greater is the susceptibility of the refractory to chemical attack by molten fluxes and gases. Decrease in porosity increases the refractory's strength and also increases its heat capacity, thermal conductivity and chemical strength.

(*viii*) Least porous bricks have highest thermal conductivity. The reason for such incidence is due to the absence of air in the void space.

Manufacturing of refractories

The steps can be displayed schematically as follows:



Common Refractory Bricks

1. **Silica bricks:** Silica bricks contain (92-95% silica, 2% lime), the main raw materials are—quartz, quartzite, sandstone etc. During manufacture, silica bricks are heated to about 1500°C within a span of 24 hours. The cooling of the bricks takes about 1-2 weeks. During heating, the quartzite converts to crystobalite. During slow cooling, crystobalite is converted to tridymite. So silica brick contains a mixture of tridymite and crystobalite. If during heating of silica bricks, quartzite is not converted to tridymite and crystobalite the bricks will expand during use in the furnace and the refractory structure will break and fall. To attain the right composition 12 hours heating at 1500°C of the bricks is very much essential.

Uses

Main applications of silica bricks are:

- In open hearth furnaces
- In coke-oven walls
- Glass-furnaces

2. **Fire clay-bricks:** Raw material is fire clay (clay–$Al_2O_3.2SiO_2.2H_2O$)

Generally fire clay bricks contain 55% silica, 35% alumina. This is acidic fire clay brick. Basic fire clay bricks contain 55% alumina and 40% silica, rest consists of K_2O, FeO, CaO, MgO.

Properties

- Light yellow-reddish brown in colour
- Low porosity and lower refractoriness than silica bricks
- Fusion temperature 1350°C
- Crushing strength 200 kg/cm^2
- Better resistance to thermal spalling than silica bricks.
- Cheaper than silica bricks.

Uses

- In blast furnaces
- In kilns
- Charging doors etc.

3. **High alumina bricks:** Composition—50% or more alumina.

Properties

- Low coefficient of expansion
- High porosity
- Little tendency to spall
- Excellent wear resistance and stability.

Uses

- For linings for Portland cement rotary kilns
- Furnace hearths and walls
- In reverberatory furnaces
- In combustion zones of oil-fired furnaces.

4. **Magnesite bricks:** Magnesite is naturally occurring magnesium carbonate ($MgCO_3$) and is the raw material for the magnesite refractories. Calcined magnesite (at 1600°C) *i.e.,* MgO is powdered to a proper size and then mixed with caustic magnesia or iron oxide as binding material and then ground. The prepared powder is pressed into bricks in hydraulic presses. The bricks are then slowly heated to 1500°C and kept for about eight hours at this temperature and cooled then slowly.

Properties

- They are generally grey or brown in colour
- They can be used upto 1500°C under a load of 3.5 kg/cm^2
- They possess good crushing strength, good resistance to basic slags and very little shrinkage
- Their resistance to abrasion is poor.

Uses

- For the lining of basic converters and open hearth furnaces in steel industry
- They are used in hot mixer linings, copper convertors
- In reverberatory furnaces for smelting lead, copper
- In refining furnaces for gold, silver and platinum etc.

5. **Dolomite bricks:** They are made by mixing calcined dolomite (*i.e.,* mixture CaO + MgO) in equimolar proportion with silica as binding material. Other binding materials used

for the same are tar, quick lime, iron oxide, clays etc. They are then fired at 1500°C for about 24 hours.

Properties

- Dolomite bricks are less strong, more porous and have more softness and shrinkage than magnesite bricks
- They can withstand a load of 3.5 kg/cm^2 at 1650°C.
- They are not very much resistant to thermal shock
- They are more resistant to slags and spalling than magnesia bricks
- They wear out quickly.

Uses

- For repairing materials
- In Bassemer converters, open-hearth furnaces, laddle-linings etc.

6. **Chromite bricks:** Chromite is a neutral refractory. The crushed chromite ore ($FeO.Cr_2O_3$) is fired at 1500°C–1700°C after mixing with a little clay as binding material.

Properties

- They are neutral in colour
- They possess high density, resistance to acidic as well as basic slags
- They can withstand upto 1800°C under a load of 3.5 kg/cm^2.
- They possess good crushing strength
- They have moderate thermal conductivities.

7. **Carborundum or silicon carbide bricks:** They are prepared from coke and sand. **Sand (60%)** and **coke (40%)** are properly mixed and is followed by addition of some sawdust and a little salt. The mixture is then fired at 1500°C in an electric furnace. Sawdust when burned evolves gases, which by circulation increases the porosity of the charge. Salt reacts with iron and similar impurities present in the raw materials to form volatile chlorides. These volatile chlorides make the final products porous. The silicon carbides obtained from the furnace are interlocked tridiscent crystals. Bonding agents like clay, silicon nitride are mixed. The mixture is then shaped, dried and fired. The firing temperature is 2000°C. At this temperature interlaced crystals are formed.

Reaction

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Composition of silicon carbide bricks is:

- Silicon = 65%
- Carbon = 30%
- Impurities = 5%

Properties

- Colour–dark grey to black
- Hardness–high
- Fusion point – 2500°C
- Coefficient of thermal expansion is very low
- Specific gravity 3.17-3.2%
- Resistance to abrassion–high

- Resistance to spallation–high
- Oxidising action–in presence of air at 1000°C silica bricks tend to oxidise to silica.

$$2SiC + 3O_2 = 2SiO_2 + 2CO$$

- Mechanical strength–very high

Uses

- Owing to its high thermal conductivity they are used in muffle furnaces.
- Owing to their high electrical conductivity, they are used in electric arc furnaces.

8. **Zirconia bricks:** Zirconia bricks fall under pure oxide refractories. Refractory oxides of common use are **alumina** (Al_2O_3), **magnesia** (MgO), **zirconia** (ZrO_2), and **thoria** (ThO_2).

Refractory oxides do not possess plastic properties. That is why clays and bentonites are to be used to prepare the pure oxide refractory bricks. Organic plasticizers such as dextrin and resins may also be used. The use of organic plasticizers makes the brick less porous.

Zirconia brick is prepared by heating zirconite (ZrO_2). First zirconia is calcined and powdered. The powdered zirconia is kept under water for sometime and the wet zirconia is mixed with binding material, *viz.* colloidal zirconia or alumina in a mill. The materials are then moulded into bricks by hand moulding or pressing. The moulded bricks are dried and fired at about 1750°C.

Properties

- Zirconia refractories fall under neutral refractories
- They can withstand a temperature upto 2600°C.
- They are resistant to basic slags.

Uses

- Zirconia bricks are very costly
- Specially used when high temperature is used

9. **Beryllia bricks:** Beryllia minerals are used to prepare the bricks which are fired at 2000°C.

Properties

- High melting point (2550°C)
- Low electrical conductivity
- High thermal conductivity
- Good resistance to thermal shocks
- Inertness to carbon dioxide and carbon monoxide upto 2000°C.

Uses

- Beryllia is used in making crucibles to melt uranium and thorium, owing to its *low neutron absorption capacity*.
- As *radiation shields* in carbon resistant furnaces.

10. **Cermets:** Cermets are hot pressed or sintered materials comprising ceramic and metallic components.

Properties

- They are the combination of ceramics and metals
- They have high refractoriness of ceramics

- They have high thermal conductivity of metals
- They have high thermal shock resistance of metals etc.
- Refractory ceramics used in the manufacture of cermets are zirconium carbide, molybdenum carbide and tungsten carbide.
- Most cermets contain about 80% of ceramic materials and 20% of the metal. They are usually fabricated by the techniques of powder metallurgy.

Uses

- In rocket and jet engine parts.
- Spinning tools for hot metals.

11. **Enamels:** Enamelling means to impart a hard and glossy coating applied on wares for decorative and protective purposes. The enamels used to coat metallic surfaces are known as *porcelain enamels*.

Raw materials used for the manufacture of enamels are:

(*i*) Refractories
(*ii*) Fluxes
(*iii*) Opacifier
(*iv*) Colours
(*v*) Floating agents
(*vi*) Electrolytes.

For making the enamel at first *frit* is made from glass forming materials such as sand, soda ash, feldspar, borax etc; when melted, they form a glass comprising sodium, potassium, calcium borosilicate.

Application of the enamel—a thin coating of the enamel thus obtained is applied on the metal either by dipping or by brushing or by pumping, then articles are fired at 800°C.

Uses

In making:

(*i*) refrigerators
(*ii*) food processing equipments
(*iii*) motor cars
(*iv*) sanitary wares.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is cement?

Ans. A cement is a substance which sets to a hard mass in presence of water.

Q. 2. What is RCC?

Ans. Concrete made with sand, stone chips and cement when reinforced with iron rod for an extra strength of the concrete is known as reinforced concrete cement (RCC).

Q. 3. What is a mortar?

Ans. The product formed after setting of lime, sand and water is known as mortar.

Q. 4. Mention the areas of application of cement.

Ans. R.C.C. walls, dams, roads etc.

Q. 5. What is a hydraulic cement?

Ans. The cement sets under water, that is why the term hydraulic came.

Q. 6. Give general composition of cement.

Ans. See text page 418.

Q. 7. What is glass?

Ans. Glass may be defined

- Physically as an amorphous, transparent or translucent, rigid supercooled liquid of infinitely high viscosity.
- Chemically as a mixture of a number of metallic silicates, one of which is an alkali metal.
- Glass has almost 100% elastic recovery.

Q. 8. What is vitrification?

Ans. The process of not forming crystals during cooling of glass is called vitrification.

Q. 9. What is devitrification of glass?

Ans. Glass-wares left unused for a long time gradually loose their transparency and become opaque due to the crystallisation of some of metallic silicates of glass. That phenomenon is known as devitrification of glass.

Q. 10. What are ceramics?

Ans. Clay materials are known as ceramics. Even at the present time ceramics remain important in many spheres of life. Building, roads, furnaces, kitchen wares, laboratory wares are made of ceramics.

The greatest uses of advanced ceramic products are in

- Aerospace industry due to their lighter weights compared to metal alloys
- Heat shields for space vehicles
- As bio materials like false teeth; bone replacement, artificial hip joints etc.

Q. 11. What are refractories?

Ans. Refractories are earthy ceramic materials of low thermal conductivity capable of withstanding extremely high temperature without any change.

Q. 12. What are primary uses of refractories?

Ans. The primary uses of refractories are for lining

(*i*) Steel furnaces

(*ii*) Coke ovens

(*iii*) Glass wares.

Q. 13. Mention some important refractories.

Ans. (*i*) Fire clay (aluminium silicates), (*ii*) Silica, (*iii*) Silicon carbide, (*iv*) High alumina (70-80% Al_2O_3), (*v*) Magnesite (MgO), (*vi*) Mullite (Clay sand), (*vii*) Zirconia (ZrO_2).

Q. 14. Mention some refractory metals.

Ans. Tungsten and tantalum (W and Ta) are refractory metals capable to withstanding high temperatures.

Q. 15. Mention some basic refractories.

Ans.

- Magnesia
- Chromite
- Forsterite.

Q. 16. Mention classification of refractories.

Ans.

(*a*) Acidic (silica, fire clay)
(*b*) Basic (magnesite, dolomite)
(*c*) Amphoteric (Al_2O_3, C, SiC).

Q. 17. What is the importance of zirconia as refractory?

Ans. Pure zirconia undergoes (*i*) a change from monoclinic crystal to tetragonal form at 980°C and (*ii*) also volume change on inversion by adding certain oxides like MgO, CaO. This type of zirconia possesses a working temperature of 2600°C.

Q. 18. Discuss the effect of heat on clay.

Ans. Clay is the common ingredient of all ceramic products, a common example is Kaolinite. At the early stages of heating, clay undergoes elimination of water of hydration at 600°C.

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow{600°C} \underbrace{Al_2O_3 + 2SiO_2}_{\text{amorphous mixture}} + 2H_2O \uparrow$$

The amorphous form of alumina changes to γ-alumina, a crystalline form at 940°C. At 1000°C, Al_2O_3 and SiO_2 combine to form mullite ($3Al_2O_3 . 2SiO_2$). As the temperature increases, more SiO_2 is converted to cristobalite. So, the overall fundamental reaction of heating of clay is

$$\underset{\text{Kaolinite}}{3(Al_2O_3.2SiO_2.2H_2O)} \xrightarrow{\Delta} \underset{\text{Mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{Cristobalite}}{4SiO_2} + 6H_2O$$

EXERCISES

1. What are silicates?
2. Define clay and soil.
3. Discuss the structural pattern of silicates.
4. What do you mean by silicate technology?
5. What do you mean by superconductive ceramics? Mention its uses.
6. Distinguish between (*a*) Pozzuolanic cement and (*b*) Portland cement.
7. How is portland cement prepared by wet process?
8. Explain the setting and hardening of cement.
9. Describe the rotary kiln used in cement manufacture.
10. Discuss the composition of Portland cement.
11. How are cements classified? Give the various physico-chemical reactions responsible for the setting and hardening of Portland cement.
12. Describe the setting of mortar and lime.
13. Describe various types of cement.

14. What are the criteria of the Portland cement raw materials?
15. What do you mean by wet and dry processes in cement manufacture?
16. How is Portland cement manufactured?
17. Describe with the help of a neat diagram of rotary kiln for the manufacture of Portland cement by wet process.
18. What is cement? Describe the composition of any cement. Briefly describe its manufacture.
19. What is glass? Discuss the physical and chemical properties of glass.
20. Classify glasses with composition and illustrations.
21. Describe the manufacture of glass by pot furnace process.
22. Write short note on soda lime glass.
23. Write notes on
  (*i*) Coloured glass
  (*ii*) Plate glass
  (*iii*) Shaping of glass
  (*iv*) Safety glass
  (*v*) Chemical action in glass making
  (*vi*) Fibre glass
  (*vii*) Annealing of glass
  (*viii*) Glass laminates
  (*ix*) Phosphate glass
24. What is glass? Write the raw materials used in the manufacture of glass.
25. Discuss the manufacture of ordinary glass with the help of flow diagram. Give reactions involved.
26. Write notes on
  (*i*) Clay and common clay
  (*ii*) China clay
  (*iii*) Fire clay
  (*iv*) Uses of clay
  (*v*) Pottery.
27. Describe the process of manufacturing of porcelain.
28. Give the reaction involved in porcelain formation.
29. What are refractories? Give an account of any four characteristics of a good refractory material.
30. Explain the theory underlying the manufacture of refractory products.
31. Describe the manufacture of:
  (*i*) Fire clay bricks
  (*ii*) Silica bricks
  (*iii*) Magnesite bricks.
32. What are basic refractories? Explain magnesite refractory in detail.
33. What are fire clay bricks? Describe the manufacture, properties and uses of fire clay bricks.
34. What are refractory materials? Write a brief note on chromite bricks.
35. Write notes on
  (*i*) Carborundum
  (*ii*) Silica refractories.
36. What are refractories? How are they classified? Give examples.
37. Explain the significance of the following properties of refractory materials
  (*i*) Porosity
  (*ii*) Dimensional stability.
38. State composition, properties and applications of the following materials:
  (*i*) Magnesite
  (*ii*) Fire clay
  (*iii*) Zirconia
  (*iv*) Silica.