

LECTURE NOTES
On
Fuel and Refractory



ORISSA SCHOOL OF MINING ENGINEERING
Government of Odisha
ଓଡ଼ିଶା ଖଣି ଯାନ୍ତ୍ରୀକ ବିଦ୍ୟାଳୟ, କେଉଁଝର

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Metallurgical Engineering Department

**Orissa School of Mining Engineering
Keonjhar**

Course code: Th3 Semester: 3rd Sem

Vision and Mission of the Department

VISION: To offer quality technical education In the field of Metallurgical Engineering with orientation towards industry, entrepreneurship, higher education and to strive for developing professionally competent technicians meeting the needs of the global economy.

MISSION:

M1 :To develop students in the field of Metallurgical Engineering as highly motivated, skillful and qualified manpower for employment and higher learning

M2 :To promote a conducive environment for all round development of students.

M3 :To promote linkages with external agencies to meet changing needs of industry and society.

M4 : To Improve Laboratories

Program Education Objectives (PEOs)

PEO 1:Diploma professionals will be able to make a successful career in metallurgical industries or higher studies to meet the needs of future requirements.

PEO 2:Diploma metallurgists will have technical and behavioral competencies through adequate exposure to industry.

PEO 3:To impart technological knowledge and skills for solving real-time engineering problems.

PEO 4:To develop human resources with capabilities of effective communication, moral values and social responsibilities

COURSE CONTENT

1.0 Fuels:

- 1.1 Define the Fuel
- 1.2 Classify the types of fuel
- 1.3 State the importance of Solid, Liquid and Gaseous fuels
- 1.4 Describe different fuels and resources of India

2.0 Solid Fuels:

2.1 COAL:

- 2.1.1 Explain the origin of coal
- 2.1.2 State the composition of coal.
- 2.1.3 Discuss the characteristics and significance of constituents
- 2.1.4 Distinguish between proximate and ultimate analysis
- 2.1.5 Define the calorific value of coal
- 2.1.6 Describe coking properties and swelling index of coal
- 2.1.7 Discuss the criteria of selection of metallurgical coal

2.2 COKE

- 2.2.1 Discuss the scope and objectives of carbonization of coal
- 2.2.2 Explain the carbonization of coal
- 2.2.3 Differentiate between high temperature carbonization and low temperature carbonization.
- 2.2.4 State the merits and demerits of H.T.C and L.T.C
- 2.2.5 Discuss different tests carried out for coke (Shatter and Micum index)

3.0 Liquid Fuels

- 3.1.1 Explain origin and constitution of petroleum
- 3.1.2 Discuss the properties of petroleum products
- 3.1.3 Discuss the distillation process of crude petroleum
- 3.1.4 Explain the production and uses of coal tar

3.1 Testing of liquid Fuels:

- 3.1.1 Define specific gravity, viscosity, flash point, cloud point & pour point, aniline point octane number and cetane number.
- 3.1.2. Discuss the methods of testing of following properties: Specific gravity, viscosity, flash point cloud point and pour point.

4.0 Gaseous Fuels:

Explain the production and utilization of following gaseous fuels:

Methane, water gas, producer gas, carbureted water gas, coke oven gas, blast furnace gas, natural gas, mixed gas.

5.0 Combustion:

5.1 Discuss the elementary principle of combustion, Hess's law of constant heat summation, Kirchoff's law.

5.2 Work out simple combustion calculation.

6.0 Refractories:

6.1 Define and Classify Refractories

6.2 Explain the desirable properties of Refractories in details

6.3 Discuss the raw materials, methods of manufacturing and properties of silica. fire clay, magnesia, dolomite, chrome magnesite graphite and magnesia carbon bricks.

1. Special Refractories

Discuss about the special refractories like high alumina, mullite, SIC, Zirconia

2. Give criteria for selection and types of refractories selected for blast furnace. LD, open hearth, arc furnace, ladle, soaking pit, coke oven, reheating furnaces, copper smelting flash and reverberatory furnaces.

1.0 FUELS

1.1 Define the fuel:

What is fuel?

A substance which produces heat is called a fuel. The heat may be produced either by combustion or by nuclear fission & fusion.

1.2 Classify the types of fuel:

Types of fuel :-

States $\left\{ \begin{array}{l} \text{(a) Solid Fuel} \\ \text{(b) Liquid Fuel} \\ \text{(c) Gaseous Fuel} \end{array} \right.$

Classification $\left\{ \begin{array}{l} \text{(a) Fossil Fuel} \\ \text{(b) Chemical Fuel} \\ \text{(c) By Product Fuel/ (co-product fuel)} \\ \text{(d) Nuclear Fuel} \end{array} \right.$

Fuels are classified mainly in 4 general classes such as

- a) Fossil fuel
- b) By product fuel
- c) Chemical fuel
- d) Nuclear fuel

(a) FOSSIL FUEL :-

Fossil fuel are those which have been divided from fossil remains of plant and animal and are found in the crust of the earth.

e.g.- Coal, Petroleum, Natural gas etc.

(b) BY PRODUCT FUEL :-

By product fuels are the co-product some regular manufacturing process. These are secondary nature of fuels.



Ex- Coke oven gas and Blast furnace gas.

(c) CHEMICAL FUEL :-

Chemical fuel are an exotic nature normally not used in conventional process.

Ex- Hydrozine (A rocket fuel)

Ammonium Nitrate, Flourine etc.

(d) NUCLEAR FUEL :-

Nuclear fuel which release heat by fission or fusion process.

(Fission –heat released by neutron bombardment) e.g: uranium, plutonium

(Fusion- heat released by fusion.) e.g:- Deuterium, Tritium (both are isotopes of hydrogen)

Depending upon the state of occurrence, fuels are classified as 3 types : –

- (a) Solid
- (b) Liquid
- (c) Gas

Fuels in each general division are further classified as

- (a) Primary and**
- (b) Secondary fuels.**

Primary fuels are those which occur in nature viz coal, wood, petroleum, natural gas etc

Secondary fuels are those which are derived from primary fuel eg fuel oil & kerosene (derived from petroleum), coke oven gas (derived from coal) etc.

Secondary fuels are further classified into

- (a) manufactured and**
- (b) by product fuels.**

Manufactured fuels are those which are made for some specific purpose

eg: coke (made for iron making) gasoline (made for internal combustion engines) producer gas (made for industrial heating) etc.

By-product fuels are those which are a co-product/side product (unavoidable product) of a regular manufacturing process.

e.g: bagasse, tar, refinery gas etc.

General Classification Of Fuel

Fuels are classified into 4 types depend upon the usages:

- (i) Domestic Fuel
- (ii) Illuminating Fuel
- (iii) Industrial Fuel
- (iv) Rocket Fuel

Domestic fuels supply heat for cooking and space heating.

Illuminating fuels e.g. kerosene, town gas etc. supply light in darkness.

Industrial fuels supply heat for process heating. steam and electricity generation etc.

Rocket fuels e.g. hydrazine are used for producing enormous thrust for the propulsion of rocket.

Features and characteristics of a good Fuel :-

- It should be readily available at cheap rate.
- It should be easy and shape to handle, store and transport and at a low cost.
- Storing and transport cost is low.
- It should have high heating value (calorific value).
- Its moisture content should be low.
- It should have moderate ignition temperature.
- Its non-combustible matter content should be low.
- It should not produce harmful product after combustion.
- It should process moderate rate of combustion.

1.3 Classification of solid, liquid and gaseous fuel:

<i>General Division</i>	<i>Primary Fuels</i>	<i>Secondary Fuels</i>	
	<i>Natural</i>	<i>Manufactured</i>	<i>By-Product</i>
Solid	Wood Coal	Semi-coke Coke Charcoal Briquette Pulverised coal	Charcoal Wood refuse Coke breeze Waste material From grain
Liquid	Petroleum	Petrol, Kerosene Alcohol, Colloidal Fuels, Fuel Oil, Naphtha, Vegetable Oil	Tar, Pitch, Benzol Paper Pulp mill waste
Gaseous	Natural Gas	Producer Gas Water Gas Carburetted water Gas, Coal Gas Oil Gas, Gobar Gas, Reformed Natural Gas, Butane, Hydrogen, Propane, Acetylene, LPG	Blast furnace gas Coke oven gas Oil refinery gas Sewage gas L.D converter gas

Rank of coal:

It denotes the maturity of coal. Coal is formed from vegetable matter which gets converted into coal via different stages of maturity.

Different stages of coal are

Immature :- [Peat → Lignite → Bituminous →

Anthracite]

Mature:- [Anthracite → Bituminous → Lignite →

Peat]

(ii) Peat is the most Immature coal, hence it is lowest rank.

(iii) Anthracite is the most mature coal, hence it is highest rank.

• COALIFICATION (Metamorphism)

The process of conversion of Lignite/ Peat to Anthracite is called Coalification.

Or

Coalification is also known as Metamorphism. The process of conversion of Lignite to Anthracite is called Coalification or Metamorphism of coal.

☆ CARBONIZATION OF COAL :-

Carbonization: heating of coal in absence of air at high temperature to produce coke is called carbonization.

Or

Heating of coal in absence of air at high temperature to produce coke is called carbonization.

GASIFICATION:-

Heating of coal with insufficiently less quantity of air plus steam to produce a gas rich in CO (carbon monoxide) and H₂ (hydrogen) is called its classification.

-This is done to produce gaseous fuel from liquid and solid fuel.

CAKING AND COKING COAL :-

□ When powdered coal is carbonized it forms an expanded lumpy mass such coals are

called, caking coal & the phenomenon is called caking of coal.

- When the residue is very hard and strong it is called caking of coal.
- All the caking coals do not form strong, hard and coherent residue coke.
- All the caking coals are essentially Bituminous Coal.
- All the caking coals do not form strong, hard coherent residue coke. Hence all the caking coals are not caking coal.

Run of mine (ROM).

The crude coal as obtained from mine is called Run of mine coals (OR) The crude (Fresh) coal as obtained from mine run of pit down to mine coal. It involves no treatment of coal, like Size Reduction, moisture elimination.

Air Dried coal- Freshly mined coals get during its storage • hence air and sun dried during its storage, various depending on the humidity and temperature of the atmospheric air. Those coals are Dried coal when the moisture is completely eliminated then the coal is completely dry and is called dry coal.

Dry ash free :-

Effect of ash and moisture in coal which is eliminated and the coal is called Dry ash free coal.

Combustion:-

It is an exothermic chemical reaction of fuel with oxygen or air to liberate heat. The quantity of heat liberated by the combustion of unit quantity of fuel is called its calorific value.

Fuel gas :-

It is the gaseous product of combustion of a fuel.

Fuel gas:- All gaseous fuels which are burnt to heat up the furnaces. Fuel gas when burnt produces flue gases.

Proximate analysis of coal:

Proximate analysis of coal means finding out the weight percentages of moisture, volatile matter, Fixed carbon and ash of coal.

This analysis gives the approximate composition of main constituents of coal and is useful to decide its utilization for a particular purpose.

Ultimate Analysis:-

Ultimate analysis means finding out the percentages of carbon, hydrogen, nitrogen, oxygen and Sulphur of the pure coal free from moisture and inorganic constituents.

Ignition temperature:-

It is the minimum temperature at which the fuel catch fire in an oxidizing atmosphere without any external source of fire.

Flash point:- It is the minimum temperature at which the liquid fuel gives enough vapour which produces a momentary flash when exposed to a flame.

Fire point:- It is the minimum temperature at which the liquid fuel vapour produces a continuous flame when exposed to a flame.

2.0 Solid Fuel

2.1 Coal:

2.1.1 ORIGIN OF COAL

Coal is a complex mixture of plant substances altered in varying degree by physical and chemical processes. These processes which changed plant substances into coal has taken million of years and has been accomplished by bacteria, heat and pressure inside the earth's crust.

Two theories namely 'in situ' theory and 'drift' theory have been suggested by the geologists regarding the mechanism of formation of coal from plant substances (e.g. wood etc.).

1. **In situ theory.** According to this theory, coal seam occupies the same site (place) where the original plants grew and where their remains accumulated several million years ago to produce coal under the action of heat, pressure and bacteria.
2. **Drift theory.** According to this theory, the plants, trees etc. were uprooted and drifted (transported) by rivers to lakes and estuaries to get deposited there to form coal during the course of time after they got buried underground. Indian coals are formed according to drift theory in general.

If sea water is the carrying agent or if the deposit is covered by marine inorganic sediments, then coal formed are rich in hydrogen and possess coking properties.

Points in favour of 'in situ' theory:

- In the existing peat deposits; the decayed vegetable matter had accumulated at the place of origin, Coal seams are found on the bed of fire clay.
- The constituents like lime, alkali, iron oxide, etc. which act as flux in such clays were found extracted by plants growing on it.
- Underclays of coal have been found to contain large quantity of fossil roots. Composition of a particular coal seam is generally constant over a wide area. Had the original decaying vegetable matter drifted from its original place, there would have been a great variation in the ash content of coal at various places in a seam
- Aquatic fossils (marine remains) are not found in coal.

Points in favour of drift theory:

- Generally, there is no sent of earth below coal and the coal has been found lying on sandstone, shale etc.
- In a coal seam, percentage of inclined trunks of fossils is much more than the vertical position. Had the coal seam been formed at the same place where the vegetable materials decayed and embedded, the fossil trunks would have been vertical.
- To form 1 metre thick coal seam, 10 metre thick seam of peat is required. So, the formation of 10 metres thick coal seam would have resulted from 100 metres thick peat seam which occurs nowhere..
- Coal seams appear like sedimentary rocks. Seams of coal are made up of different layers separated by layers of shale, clay or sandstone which vary in thickness from a mere film to several metres.

The stages in the formation of coal from vegetable/plant (wood) matters are as follows:

- ❖ Plant debris (wood) peat→ lignite→ brown coal →sub-bituminous coal→ bituminous coal→ semi anthracite coal → anthracite coal→ graphite.
- ❖ This process of coal formation may be complete or may be stopped at any stage giving rise to coal of varying maturity which is implied by the term '*rank' of the coal.*
- ❖ In this series from peat to anthracite; each member is more mature or of higher rank than the one which precedes in the series. Thus anthracite coal is of higher rank than bituminous coal, Bituminous coal is of higher rank (ie, more mature) than lignite. With the progress of coal forming reaction, moisture and oxygen content reduces and percentage of carbon increases. Also the calorific value increases from 4500 kcal/kg for lignite to 8500 kcal/kg for bifuminous coal.
- ❖ There is a slight fall in the calorific value of anthracite coal because of removal of hydrogen.

The effect of depth of occurrence on the maturity of coal is obvious. Both temperature and pressure rise with the increase in depth and the rate of a chemical change doubles for a rise of about 10°C. Hence the coals in the lower seams of coal measures are generally more mature than those of higher seams. This variation of rank with depth is known as Hill's law. Temperature gradient in earth's crust in India is about increase of C/30 m depth.

The precise nature of the changes that took place in the gradual conversion of plant material into coal is not known but it may be inferred that the bacterial attack in the first stage of coal formation brought about chemical reactions under oxidising atmosphere, in which all the ingredients of plants took part and produced the humic acids and other components of peat. Later peat was buried under mineral rocks and pressed into more and more compact material. Chemical reaction (such as dehydration, decarboxylation, dehydrogenation etc.) took place with the result that H₂O, CO₂, CH₄, and H₂S were removed off and the humic acids of peat were converted more and more into neutral substances. The result was lignite. In contrast to the biochemical stage, the lignite formation passed through a reducing atmosphere. The aging of lignite into bituminous and anthracite coals was due to further reduction and condensation reactions. Generally, with the increase of vertical depth, the carbon content of the coal increases and the volatile matter decreases.

The process of coal formation (called coalification or metamorphism) may be complete or may be stopped at any stage, thus giving rise to coals of varying maturity represented by the term "rank of coal"

Different stages in the formation of coal from plant/vegetable debris (called peat to anthracite series) is as follows:

Plant/vegetable debris → peat → lignite → sub-bituminous coal → bituminous coal → semi-bituminous coal → semi-anthracite coal → anthracite coal → graphite "

Each member is more mature (i.e. of higher rank) than the one which precedes it in the series. Thus, anthracite coal is of higher rank than bituminous coal.

Generally, as the coalification (i.e. maturity of coal) progresses, the moisture and oxygen percent in the coal decreases whereas the carbon content and the heating value increases. Heating value of anthracite coal may be slightly less than that of bituminous coal due to the removal of hydrogen.

2.1.3 Characteristics of different coals:

PEAT:

- It is the first stage product in the formation of coal from wood under the action of temperature, pressure and bacteria. Freshly dug peat contains large amount of water (upto 90%), hence it is sun dried before using as a fuel.
- Its calorific value is (around 4500 kcal/kg) slightly higher than that of the wood.
- Near the surface of the deposit, peat is light brown in colour and highly fibrous nature. With the increase in the depth, the colour becomes darker and finally black) when

vegetable structure is not so obvious.

- It is mainly used as a domestic fuel as well as for power generation.
- It is easy to ignite and burns freely with long flames.
- Peat is also used as a fertilizer or for making fertilizer.

- Composition-

- *Proximate analysis:*

Moisture: 15-25%

Ash: 3-10%

Volatile matter: 50-55%

Fixed carbon: 25-30%

Ultimate analysis:

carbon:55-60%

Hydrogen: 6-6.5%

oxygen: 30-35%

nitrogen: 1.5-2%

LIGNITE

- It is the second stage product in the formation of coal from wood. It is friable and occurs in
- Thick seams (up to 30 metres thickness) near the earth's surface.
- Its moisture content is upto 60% and calorific value around 5000 kcal/kg (on 10% moisture basis).
- Colour is brown (darken brown).
- It is likely to ignite spontaneously as it adsorbs oxygen readily and must not be stored in the open without care.
- *Proximate analysis:*
 - Moisture content-10-30%
 - Ash – 3.5-7.5%
 - Volatile matter- 40-45%
 - Fixed carbon- 30-35%
- *Ultimate analysis:*
 - Carbon- 70-73%
 - Hydrogen - 4.6-6.5%
 - Oxygen - 22-26%
 - Nitrogen - 0.6-1.5%
 - Sulphur - 0.6-1.5%
- Its extensive deposits occur in the U.S.S.R., U.S.A., Germany, Australia, Canada and India.
- The major deposit of true lignite in India is in Neyveli in Tamil Nadu (2000 million tons). Nichahom (Kashmir), Kerala coasts, Palana and Khari (Rajasthan) and Umarsar (Gujarat) have smaller deposits.
- The lignite deposits in many areas are relatively near the earth's surface and are quite thick. The deposit of Neyveli occurs about 60 m below the ground level and is 15-20m thick.

Uses of lignite:

- Lignite is used in the generate of electricity in thermal power station.
- Other uses of lignite are in gas production and metallurgical furnaces.
- Lignite is extensively used in the manufacture of producer gas.
- It is also gasified into synthesis gas for ammonia production.

SUB-BITUMINOUS COAL

- It is a black, homogeneous and smooth mass having high moisture and volatile matter content
- which breaks into smaller pieces on exposure to air Its carbon content is around 70-80% and
- oxygen content is 10-20%.
- It is a non-coking coal having a calorific value about 7000 kcal/kg
- It is a variety of mature lignite resembling true coal in colour and appearance.
- It is black in colour with a dull, waxy lustre.
- It is denser and harder than lignite and has a lower moisture content.
- Most sub-bituminous coals appear banded like bituminous coal.
- It is occurs in the USA, USSR, GERMENY and austrelia.

Proximate analysis:

- Moisture content-10-20%
- Ash – 3.5-7.5%
- Volatile matter- 40%
- Fixed carbon- 30-35%

Ultimate analysis:

- Carbon- 70-80%
- Hydrogen - 4.5-5.5%
- Oxygen - 22-26%
- Nitrogen - 20%

Uses of lignite:

It ignite easily and is used in raising steam.

For manufacturing gaseous fuels also, if low in sulphur.

BITUMINOUS COAL

- It is the most common variety of coal known as Koela" in Hindi.
- It is black & brittle which burns & ignites readily with yellow smoky flame.
- It has low moisture content (< 10%) and the carbon content varies from 75-90% whereas the volatile matter content is 20-45% .
- Depending upon the volatile matter content, it is termed as low volatile, medium volatile and high volatile coal.
- Bituminous coal is black and usually banded, the bands being parallel to the bedding

plane.

- The luster varies from bright to dull. Bituminous coal is denser and harder than lignite and sub-bituminous coal and does not disintegrate into slacks on exposure to the atmosphere.
- Most of the coking coals are essentially bituminous coal.

Proximate analysis:

- Moisture content-10%
- Ash – 1.2%
- Volatile matter- 20-45%
- Fixed carbon- 75-90%

Ultimate analysis:

- Carbon- 80-90%
- Hydrogen - 0.5-1.5%
- Oxygen - 22-26%

Uses of lignite:

- It is used for power generation, coke making, gasification coke making which requires coking coal.
- It is used for combustion in domestic ovens, industrial furnaces and boilers, railway locomotives and thermal power station.
- Two other important uses are carbonization and gasification where by coal is converted into solid fuels (coke, semicoke) ,gaseous fuel (producer gas, water gas, coal gas) and liquid fuels(e.g. coal tar fuel)
- It is also a source of a wide range of coal chemicals, fertilizers and synthetic liquid fuels.

Table 4.6. Typical Composition and Properties so some Indian Bituminous Coals

Coalfield	Basis-Air-dried, %			Basis : d.m.m.f., %				Calorific value kcal / kg (d.m.m.f.)	Caking properties
	Moisture	Ash	Volatile matter	Carbon	Hydrogen	Nitrogen	Oxygen		
Raniganj, Dishergarh	2.5-3.5	15-20	39-44	83-85	5.3-5.8	2.0-2.3	8.0-9.0	8100-8500	Caking
Jharia, Mahuda	1.5-2.2	20-25	36-40	85-87	5.4-5.8	1.7-2.2	3.9-7.5	8400-8600	Caking
Giridih, Karharbari	0.6-1.3	12-22	27-33	89-92	4.7-5.2	1.6-1.9	0.6-2.4	8700-8900	Caking
East Bokaro, Jarangdih	0.8-2.4	13-21	28-36	85-90	4.5-5.4	1.8-2.0	4.0-8.0	8300-8700	Caking
West Bokaro, Kuju	4.2-4.7	14-19	34-37	84-86	4.9-5.1	1.9-2.2	6.0-8.0	8200-8400	Caking
Singrauli	7-9	16-24	37-45	78-81	4.4-5.3	1.5-1.8	12-14	7600-7800	Noncaking
Korba	6-9	12-38	28-41	81-85	4.5-5.3	1.8-2.0	8-12	7800-8200	Noncaking
Wardha Valley, Ballarpur	6-10	12-30	35-42	80-83	4.5-5.0	1.6-2.0	12-14	7300-7900	Noncaking
Talcher	7.0	18-28	41-44	79-82	4.9-5.3	1.6-1.8	10-12	7800-7900	Noncaking

Semi- Anthracite Coal :

- Its properties lie between that of bituminous and anthracite coal.
- it is harder than the most mature bituminous coal and ignites more easily than anthracite to give a short flame changing from yellow to blue.
- Calorific value of semi anthracite 8500-8800 kcal/kg.
- it is a non-coking coal.
- The semi anthracite coal do not occur in india.
- Its moisture content to around in 1-2%.

proximate analysis:-

Moisture content – 1-2%

Volatile matter – 10- 25%

Anthracite coal:

- This is the most mature coal , hence is the highest rank thus high carbon content (85-90) and low volatile matter (<10%) coal is hard , non- luminous flame there - by imparting intense localized heating .
- it ignites with difficulty due to low volatile matter content.
- It has subshell metal, sometimes even a graphitic appearance .
- Proximate analysis :-
 - ultimate analysis
- low volatile matter – 3-10%
 - carbon – 92%
- Moisture content – 2-4%
 - hydrogen -2.8 – 3.9 %
- Calorific value of Anthracite 8000-8500 kcal/kg .
- Most deposits of anthracites are in south and pennsylvania (U.S.A).
- True anthracites do not occur in india .
- It burns with without smoke with a short non luminous flame .
- It is a non – coking coal .

Uses:-

- The chief uses of anthracite are in boiler , domestic oven and metallurgical furnaces . It is also used in small quantities as a component of coke oven charges .on calcining it gives thermos – anthracite which is a raw material for the production of carbon electrodes.

Deposits:

- The most notable deposits of anthracite are in south wales (u.k)and pennsylvania (u.s.a)
 - Three anthracites do not occur in india .
 - The tertiary coal in jammu and lower and wana coals in darjeeling have properties approaching those of anthracites and are known as anthracites and are known as anthracites coals .
 - Proximate analysis:-
 - V.M =10 % less than

2.1.2 Significance of the various constituents of coal:-

➤ **Moisture**

Moisture in general, high moisture content in coal is undesirable because

- I. It reduces the calorific value of the coal.
 - II. It reduces the consumption of coal for heating purpose.
 - III. It lengthens the time the timing of heating.
 - IV. We pay for it when the coal is purchased and transported. But there are certain specific cases where moisture is deliberately added or is desirable to some extent.
- Dust nuisance is checked while loading, unloading, transporting and charging of the hot coal bed thereby eliminating its fusion and clinked formation which otherwise would have blocked the passage of air.
 - Sometimes, water is sprayed on the coal dust charged in the coke oven.
 - Moisture undergoes endothermic decomposition to reduce the temperature of the coke oven gas as well as that of the coke mass thereby eliminating its fusion.
 - Coal/coke absorbs moisture due to rain, quenching or washing.

➤ **Volatile Matter**

- Volatile matter is not a constituent of coal. It represents the volatile products of thermal- decomposition of coal under specified condition.
- Volatile matter is the loss of weight of coal when heated in absence of air for a standard time at standard temperature.

The coal with higher volatile matter content :-

- Has lower calorific value.
- It requires larger furnace volume for its combustion.
- It decreases the maturity of coal.

Benefits :-

- It ignites easily. That means it has lower ignition temperature.
- Volatile matter burns with long smoky yellow flame.
- Volatile matter will give more quantity of coke oven gas.
- Volatile matter has a high temperature catching fire.

➤ **Mineral matter and ash :-**

- Ash is the combustion product of mineral matters present in the coal.

Mineral matter –

- It consists of silica (SiO₂), Alumina (Al₂O₃), and ferric oxide (FeO) with varying amount of other oxides such as calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na₂O) etc.
- High ash content in coal is undesirable because;
 - a) The coal with high ash content is harder and stronger.
 - b) High ash coal has lower calorific value. It produces more slag in the blast furnace when coke made up in.

Ash content of the coal is reduced by its washing :-

- Mineral matter content should be low in between 2 to 3 or less in all coal.

$\text{Mineral Matter} = 1.08 \times \text{ash} + 0.5 S$
$\text{In India (Mineral Matter)} \rightarrow = 1.1 \times A$

Empirical formula are available to calculate the mineral matter content form the ash(A) values.

➤ Fixed Carbon :-

- It is the pure carbon present in the coal. Higher the fixed carbon content of the coal, higher will be calorific value.
- The carbon content of coal increases with increasing of coal.

➤ Total Carbon :-

- It means the fixed carbon plus the carbon present in the volatile matter CO, CO₂, CH₂.
- Total carbon is always more than the fixed carbon.
- In anthracite volatile matter is very small and the value of fixed carbon and total carbon are almost equal.

➤ Hydrogen :-

- It is the increase calorific value of coal.
- The percentage of NH₃ is recovered as (NH₄)₂SO₄ which is a valuable fertiliser.
- The content of hydrogen in coal from the peat to bituminous stage varies between 4.5 to 6.5% and is not related to the rank.
- Beyond the Bituminous stage, the hydrogen content shaply decreases to a value of 1-2% in anthracites.

Ex-- Canal coal has – Low H₂ content

Boghead coal has – High H₂ content

➤ **Nitrogen :-**

- Presence of inert nitrogen decreases the calorific value of the coal.
- It is more between 1-2%.
- When coal is carbonised the nitrogen and hydrogen combine and produced ammonia.

➤ **Sulphur :-**

- Though its presence increases the calorific value of the coal but it has several undesirable effects.
- It's oxidation product of sulphur (SO_2 , SO_3) especially in presence of moisture cause corrosion.
- Sulphur is highly undesirable in metallurgical coal used in iron and steel making.
- As it badly affects the properties of iron and steel.
- It causes hot shortness of steel (Cracking of steel) surface during hot rolling.
- Indian coals are usually low in sulphur ($\leq 0.7\%$). But the majority of the coals in Assam coalfields have high sulphur (around 4%).

➤ **Oxygen :-**

- The less the oxygen content the better is the coal as it reduces its calorific value.
- It decreases from lignite to anthracite as the maturity of the coal increases.
- As the oxygen content increases, its moisture holding capacity increases and the caking power decreases.
- An increase of 1% in oxygen content of coal, reduces the calorific value of Bituminous coal by 1.7%.

Ex-- Vitrinite coal – High oxygen coal

Exinites coal – Intermediate Oxygen coal

Fusinite Coal – Lowest oxygen Coal

➤ **Phosphorous :-**

- It is undesirable in metallurgical coal. As it badly affects the properties of steel and causes cold shortness of steel. Cracking of steel surface during cold rolling.
- Indian coking coals have normally less than 0.5% of phosphorous.

➤ **Chlorine :-**

- It is present mainly as chlorine in the coal.
- It reduces the fusion point of the ash of the coal.

Assignment

Q. Write down the uses of different coal samples.

Uses of Coal :-

- Directly burning and getting heat.
- Generating Steam for producing electricity.
- Driving railway locomotives.
- Manufacturing coke and coal gas (coke oven gas, producer gas, water gas)
- Manufacturing synthetic liquid fuels.
- Gasification to produce nitrogenous fertiliser from synthetic gas.

Uses of Bituminous and lower rank coals :-

- Production of activated carbon used for decoloration of glycerine and petroleum products.
- Treatment with strong sulphuric acid forms a basic exchange agent used in water treatment process.
- Used as pigments for paints.
- Powdered coal is used in dynamite.
- Used as filter for various products due to its higher chemical inertness and low cost.
- Used for making carbon brushes.
- Used for burning in domestic oven.
- Carbonisation of bituminous coal produces chemicals such as coke. It is also briquetted and used host of other chemicals.

Uses of Peat :-

- It can be carbonised to produce gas and coke. It is also briquetted and used as a domestic fuel.

Uses of Lignite:-

- For manufacture of producer gas.
- For generation of electrical power.
- For gasification to produces nitrogenous fertiliser.

Uses of Anthracite Coal:-

- For recarbonising.
- For making carbon electrodes, brushes, butterfly parts carbon refractory, corrosion resisting structural materials.
- As filter and paint pigment.

- For blending with coking coal to check its swelling and improving the coke equality.

2.1.4 Properties and Testing of coal :-

➤ Proximate analysis of coal:-

Determination of moisture, volatile matter, ash and fixed carbon in coal comprises its proximate analysis.

Determination of moisture content in coal:-

- Loss in weight of coal caused by heating of weight quantity of coal Sample for one hour at 105⁰C is the moisture content in coal.
- The percentage of moisture is given by

$$\% \text{ Moisture in coal} = (\text{Loss in weight of coal} / \text{Weight of coal initially taken}) \times 100$$

Determination of Volatile Matter in coal:-

- It is the loss in weight of moisture free powder from when heated in a crucible fitted with cover a muffle furnace at 950⁰C for 7 minutes.

$$\% \text{ Volatile matter} = (\text{Loss in weight of Moisture free coal} / \text{Weight of moisture free coal}) \times 100$$

Determination of Ash in coal:-

- It is the weight of residue after burning a weighed quantity of coal in an open crucible (In presence of air) at 750⁰C in a muffle furnace till a constant weight is achieved.

$$\% \text{ Ash in coal} = (\text{Weight of residue ash formed} / \text{Weight of coal initially taken}) \times 100$$

Determination of Fixed Carbon :-

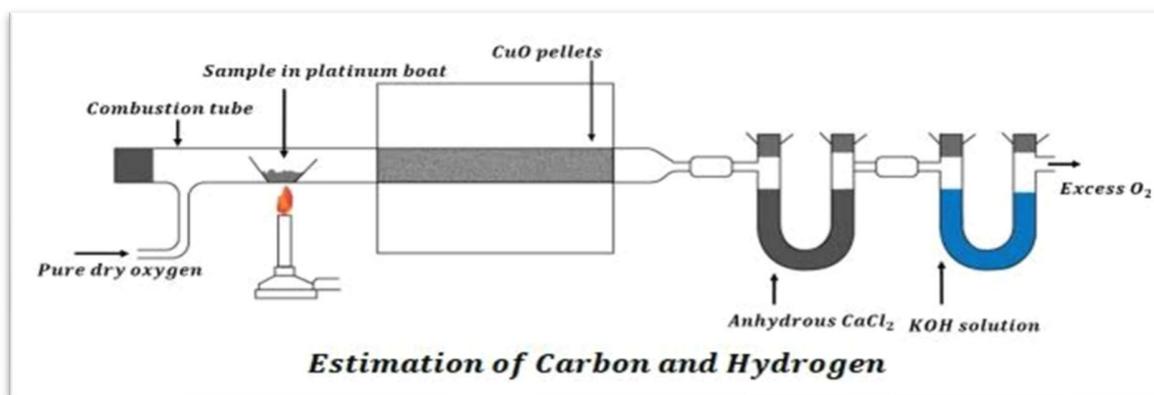
- It is determined indirectly by deducting the sum total of moisture, volatile matter and ash percentage from 100.

$$\% \text{ Fixed Carbon in coal} = 100 - (\% \text{ Moisture} + \% \text{ Volatile Matter} + \% \text{ Ash})$$

Ultimate Analysis of Coal :-

Determination of total carbon, hydrogen, nitrogen, oxygen, and sulphur percentage in coal comprises its ultimate analysis.

(1) Determination of Carbon and Hydrogen in coal :-



A known amount of coal is burnt in a current of dry oxygen thereby converting C and H of coal into CO₂ (C + O₂ = CO₂) and H₂O (H₂ + ½O₂ = H₂O) respectively. The products of combustion (CO₂ and H₂O) are passed over weighed tubes of anhydrous calcium chloride and potassium hydroxide which absorb H₂O and CO₂ respectively. The increase in the weight of CaCl₂ tube represents the weight of water (H₂O) formed while increase in the weight of KOH tube represents the weight of CO₂ formed.

% of H and C in coal be calculated as below,

Let, x = weight of coal sample taken

Y = increase in the weight of CaCl₂ tube

Z = increase in the weight of KOH tube

$$\therefore \text{Amount of carbon in the coal sample} = \frac{12}{44} \times z$$

[since, 44 gm of CO₂ is product from 12 gm of carbon and 32 gm oxygen => C(12) + O₂(32) = CO₂ (44)]

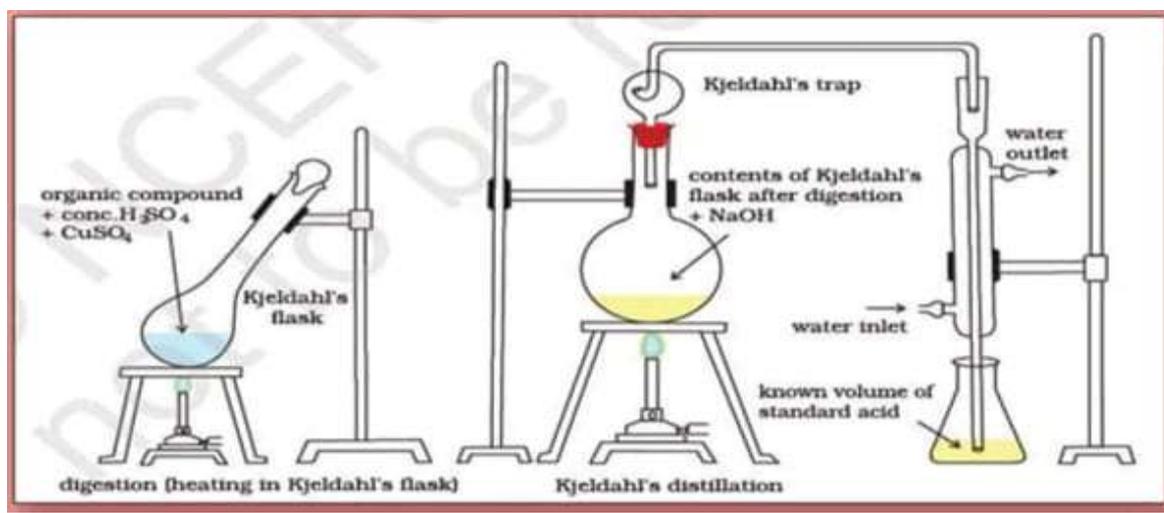
$$\therefore \% \text{ carbon in coal} = \frac{12 \times Z}{44 \times X} \times 100$$

Similarly, amount of hydrogen in coal sample = $\frac{2}{18} \times y$

[since, 18 gm of water is formed by 2 gm of hydrogen and 16 gm oxygen = H₂ + ½ O₂ = H₂O]
2 16 18

$$\% \text{ Hydrogen in coal} = \left(\frac{2 \times Y}{18 \times X} \right) \times 100$$

2. Determine the nitrogen in coal:-



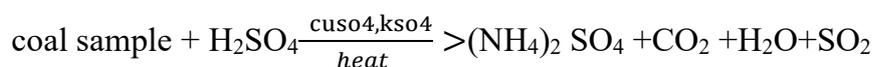
Nitrogen estimation in coal is done by Kjeldahl's method. A known weight of powdered coal is heated with concentrated sulphuric acid in presence of potassium sulphate and copper sulphate in long necked flask (called kjeldahl's flask) thereby converting nitrogen of coal to ammonium sulphate. When clear solution is obtained (i.e. when whole nitrogen is converted in to ammonium sulphate) it is treated with 50% NaOH solution. The ammonia thus formed is distilled over and absorbed in known quantity of standard sulphuric acid solution.

The volume of unused sulphuric acid is determined by titrating against standard NaOH solution.

Thus, the amount of acid neutralized by liberated ammonia (from coal) is determined .

Reaction of Nitrogen (N₂) :-

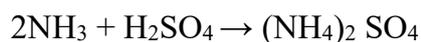
(i) Degradation / Digestion –



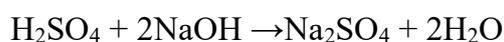
(ii) Liberation of NH₃- (dissolution flash)



(iii) Absorption of NH₃ :- (Condenser tube)



(iv) Titration of H₂SO₄ - (In test tube)



CALCULATION:

$$\% \text{ in nitrogen in coal} = \frac{\text{volume of acid used} \times \text{Normality}}{\text{weight of coal taken}} \times 1.4$$

since, $(\text{NH}_4)_2 \text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{NH}_4\text{OH}$

One liter of N/10 H_2SO_4 consumed is equivalent to 0.1gm mole of ammonia or 1.4gm of nitrogen.

volume of acid used = $V_1 - V_2$

where, V_1 = Volume of H_2SO_4 neutralised in blank, c.c

V_2 = volume of H_2SO_4 neutralised in determination, c.c

Determination of Sulphur in coal :-

A known quantity of coal is burnt completely in bomb calorimeter in a current of oxygen. Ash, thus obtained contains sulphur of the coal as sulphate which is extracted with dilute hydrochloric acid and the acid extract is treated with barium chloride solution to precipitate the sulphate as barium sulphate.

Reactions:

1) $\text{Coal} + \text{O}_2 \rightarrow \text{Ash}$



2) $\text{Ash} + \text{H}_2\text{O} \rightarrow \text{Sulphur present in the form of sulphate}$



3) Sulphate is extracted with dilute HCL



CALCULATION:

Let, wt of $\text{BaSO}_4 = x$ gm

Wt of initial coal = w gm

233gm of BaSO_4 has \rightarrow 32gm of 'S'

x gm BaSO_4 has = $\frac{32}{233} \times x$ gm 'S'

$$\% \text{ of Sulphur} = \frac{\frac{32}{233} \times x}{w} \times 100$$

Determination of % Oxygen & % Ash :-

$$\% O_2 = 100 - (\%C + \%H_2 + \%N_2 + \%S + \%ash)$$

$$\% Ash = \text{weight of ash formed} / \text{initial weight of coal} \times 100$$

Problem :-

1.56 gm of coal sample was kjeldahlised and NH_3 gas thus evolved in 50ml of 0.1N H_2SO_4 observed on the excess (residue) acid required 6.25 ml of 0.1N NaOH for exact neutralization . Calculate the %N in coal sample?

Ans :-

$$\%N = \text{volume of acid used} \times \text{normality} / \text{weight of coal sample taken} \times 100$$

Given data ,

$$\text{weight of coal sample} = 1.56\text{gm}$$

$$\text{Acid} = H_2SO_4$$

$$\text{Normality} = 0.1N$$

$$\text{Volume of acid} = 50\text{ml}$$

$$\text{Residue of acid} = 6.25 \text{ ml}$$

$$\text{Volume of acid used} = 50 - 6.25$$

$$= 43.75\text{ml}$$

$$\%N = 43.75 \times 0.1 \times 1.4 / 1.56$$

$$= 3.92\% \text{ (Ans)}$$

CALORIFIC VALUE:

It is defined as the quantity of heat liberated by combustion of unit quantity of fuel.

It is 2 types.

(1) Gcv

(2) Ncv

Gross calorific Value-

(higher c. v) Net calorific

Valur (lower c. v)

$$\square \text{ GCV} = (\text{NCV} + \text{Latent heat})$$

$$\square \text{ NCV} = (\text{GCV} - \text{catent heat})$$

Principle of CV. Determination-

when a weighed quantity of fuel is burnt in the calorimeter, the heat liberated is used up in heating the calorimeter and the water in the calorimeter. By equating the heat given out by

the fuel with heat taken up by the calorimeter and water, the calorific value (also called heating value) is Determined.

It is of two types :-

- Gross Calorific Value-higher calorific value.
- Net calorific Value-Lower calorific value.

Higher And lower calorific

Value:-

- Higher calorific value :-
- Higher on gross calorific Value (other name)
- Hydrogen is found to be present in almost fuels.
- fuel is determined hydrogen is converted in to steam.
- The products of combustion are at room temperature in 25°C.
- The latent heat of condensation of steam also gets included in the measured heat.
- The total calculated value is higher or gross calorific value.
- *GCV may be defined as the total amount of heat liberated when one unit of the fuel burnt completely and the combustion products are cooled to room temperature.*

Lower Calorific Value :-

- Lower or Net calorific value.
- The water vapors escape as such the hot combustion gases.
- *NCV may be defined as the amount of heat liberated when one unit of the fuel is burnt completely and the combustion products are allowed to escape here.*

- **Net C. V= Gross CV- Latent heat of water vapors formed.**

2.1.5 Determination of calorific value by Bomb calorimeter :-

Bomb calorimeter is used for determining the calorific of solid and liquid fuels.

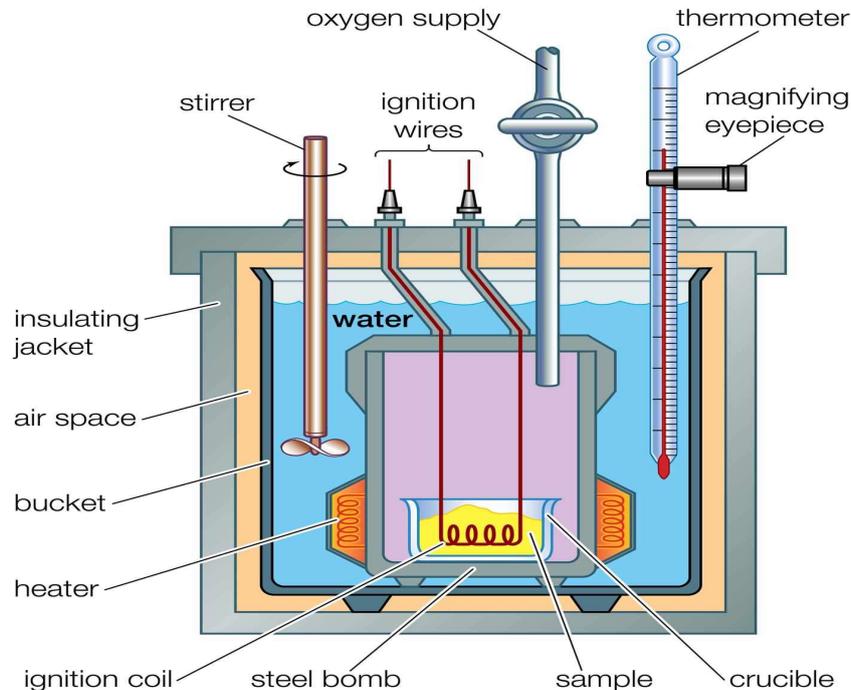


Fig: BOMB CALORIEMETER

WORKING-

- A weighed amount of the fuel is placed in the silica crucible. The crucible is supported over the ring.
- A fine magnesium wire touching the fuel sample is stretched across the electrode.
- Oxygen supply is forced into the bomb till a pressure of 25-30 atmospheres is reached.
- Initial temperature of the water in the calorimeter is noted after thorough stirring.
- The current is switched on the fuel in the crucible burns with the evaluation of heat.
- The heat produced by burning of the fuel is transferred to water which is stirred throughout the experiment by the electric stirrer. Maximum temperature by the thermometer is recorded.
- The calorific value of the fuel can now be calculated as below

Observations;-

weight of the fuel taken in crucible = x kg

Weight of the water in the calorimeter water = y kg

water equivalent of the calorimeter, stirrer, thermometer and bomb = Z kg.

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

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

Let, The higher (gross) calorific Value of the fuel = C kcal/kg

Calculations –

Heat gained by water = $y \times (t_2 - t_1)$ Kcal.

Heat gained by calorimeter = $Z \times (t_2 - t_1)$ Kcal

Total heat gained = $y (t_2 - t_1) + z (t_2 - t_1)$ Kcal

= $(y+z) (t_2 - t_1)$ Kcal

Heat liberated by fuel = $x \times C$ Kcal

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

$$x \times C = (y + z) (t_2 - t_1)$$

$$\square \text{ gross calorific value} = C = \frac{(y+z) (t_2 - t_1)}{X} \text{ Kcal/kg.}$$

Calculation of lower (net) calorific value:

Let the percentage of the hydrogen in fuel = H

Weight of water produced from 1 gm of fuel = $9H \div 100$ gm = $0.09H$ gm.

Heat taken by the water in forming steam = $0.09H \times 587$ kcal. (Because of latent heat steam = 587 kcal/kg.

Hence, lower (net) calorific value of fuel = higher calorific value - latent heat of water vapor formed

$$\text{NET C.V} = (C - 0.09H \times 587) \text{ Kcal/Kg}$$

2.2 COKE

2.1.1 Carbonisation:

Heating of coal in absence of air to produce coke is called its carbonisation or destructive distillation. Its main purpose is to produce coke whereas the co-product is called coke oven gas from which various liquid products like tar, benzol, naphthalene, phenol, anthracene etc. are separated.

Types of Carbonisation: There are mainly two types of carbonisation depending upon the temperature upto which the coal is heated in absence of air.

1. Low temperature carbonisation (LTC) and
2. High temperature carbonisation (HTC).

2.1.3 Difference between LTC & HTC.

<i>Low Temperature Carbonisation (LTC)</i>	<i>High Temperature Carbonisation (HTC)</i>
(a) It is carried out at 700°C.	(a) It is carried out at 1100°C.
(b) It produces semi-coke which is used as a smokeless domestic fuel. It can sometimes be used in boiler also to avoid smoke.	(b) It produces metallurgical coke for use in blast furnace and cupolas in foundry etc.
(c) Yield of coke oven gas is less in LTC. It is about 150-160 Nm ³ gas/ton dry coal. Less gas yield is due to less devolatilisation of coal and less cracking of hydrocarbons at lower temperature of carbonisation.	(c) Yield of coke oven gas is more in HTC due to more cracking of hydrocarbons (mainly methane in coke oven gas) at higher temperature. Yield is about 250-300 Nm ³ /ton of dry coal.
(d) Yield of tar is high in low temp. carbonisation. It is about 10% of dry coal.	(d) Tar yield is less here. It is about 3% of dry coal charged.
(e) Ammonia yield is low.	(e) Ammonia yield is more (10-15 gm/Nm ³ of coke oven gas)
(f) Calorific value of coke oven gas produced in LTC is more due to higher percentage of methane and unasturated hydrocarbons in it. C.V. is about 6000-6500 kcal/Nm ³ .	(f) C.V. of coke oven gas produced in H.T.C.es. It is about 4200-4400 kcal/Nm ³ only due to lesser percentage of hydrocarbons resulting from its tracking at higher temperature of carbonization.
(g) The tar produced is aliphatic in nature. It contains less quantity of aromatic ring compounds like benzene, toluene, naphthalene, phenol, anthracene etc. However, tar acid content is higher. The produced in called	(g) Tar produced has more of aromatic ring compounds. (due to crystallisation reaction of straight chain compounds being favoured at higher temperature).

primary tar and has a low or market value than high temp tar.

(h) After carbonisation, discharging of coke is difficult as it swells a lot but does not shrink much finally at the end of coking due to lower of carbonization.

(i) Free carbon in tar (which results from the cracking of hydrocarbons) is less. It is about 5-10% of tar. Since cracking ($\text{HC} \rightarrow \text{H} + \text{C}$) is less severe at lower temperature.

(j) Coke produced is weaker (due to less shrinkage), bigger in size and more reactive (due to higher porosity). Coke produced is termed as soft coke.

(k) Volatile matter content in coke is more (5-7%) hence it is easier to ignite it because of lower ignition temperature of high volatile matter containing coke. Ignition temperature of LTC coke is about 425°C .

(l) Hydrogen content in coke oven gas is less (35-40%). Hence, difference in gross and net calorific value is less.

(m) Coke yield is more. It is about 80% of dry coal.

(n) Density of coke oven gas produced is more, i.e. about 0.65 kg/Nm^3 .

(h) Discharging of coke from ovens is easier as it shrinks finally to a more extent comparatively due to higher temperature of carbonisation.

(i) Free carbon in tar is more (due to more intense cracking of hydrocarbon at higher temperature. It is about 15-20% of tar. Higher carbon in tar chokes the hydraulic main and other tar flow pipelines).

(j) Coke produced is stronger (i.e. shatter index, micum index, abrasion index are more), smaller in size and less reactive (due to low porosity) due to higher amount of shrinkage of coke at higher temperature. Coke produced is called hard coke.

(k) V.M. in cake is less (1-2%), hence its ignition temperature is more Ignition temperature of high temp coke is about 600°C .

(l) H_2 content in coke oven gas is more (55–60%). It is beneficial for an adjoining nitrogeneous fertiliser plant attached to steel plant (as in the case of Rourkela Steel Plant) which gets hydrogen (for ammonia making) from coke oven gas by its cryogenic cooling.

(m) Cake yield is less (about 75% of dry coal).

(n) Density of coke oven gas produced is less i.e. about 0.45 kg/Nm^3 .

2.1.2 Physio chemical changes during carbonization of coal:

Temperature, °C	Effect	Nature of product		
		Carbonaceous residue (solid)	Tar and Oil	Gas
300	Initial decomposition temperature	Coal	Nil	Some CO + CO ₂ , H ₂ O
320	Slight appearance of oil	Coal	Thin, light coloured oil	Above plus some CH ₄ and unsaturated hydrocarbon
360	Marked evolution of thick coal, oils and hydrocarbon gases, coal residue begins to soften	Partially softened	Darker, red or brown oil.	More CH ₄ , and higher paraffins, some H ₂
430	Evolution of viscous oil and tar. Coal residue becomes softer and swells. Pronounced gas evolution causes bubble formation, rapid decomposition of coal.	Soft carbonaceous mass of maximum volume and bubble structure.	Darker brown more viscous oil.	Maximum evolution of paraffin and unsaturated hydrocarbons with some CO, H ₂ , and H ₂ O.
460	Oil and tar yield reduces, plastic expanded mass solidifies to semi-coke.	Solid semicoke with maximum bubble structure and weak cell walls.	Nearly viscous oil or tar	
600	Oil and tar cease, hard semi coke starts to shrink.	Semicoke is harder and shrinken, colour is still black.	Non-evolved	Diminishing yield of hydrocarbons water, some in CO and H ₂ O.
900-1050	Continued shrinkage hardens the coke, structure changes with commencement of formation of graphite lattice.	Hard, silvery, grey appearance	Non-evolved	Gasses namely CO, H ₂ , and CH ₄ .

Hence mechanism of coal carbonisation may be summarised as occurring in three stages.

Stage-I.

Primary breakdown of coal at 700°C yields decomposition products like H₂O, CO, CO₂, H₂S, aromatics paraffins, olefins, phenolics, nitrogen containing compounds etc.

Stage-II.

Secondary thermal reaction among these liberated primary products as they pass through hot coke, along hot oven walls and through highly heated free space in the oven involve both synthesis and degradation. Evolution H₂, and formation of aromatics and methane occur at 700°C.

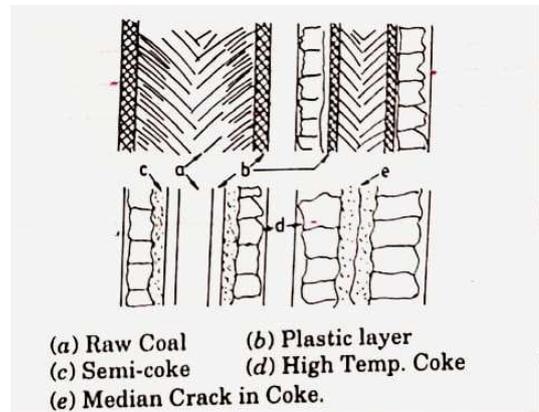
Decomposition of complex nitrogen containing compounds produces NH₃, HCN, N₂ and pyridine bases.

Stage-III.

Progressive removal of hydrogen from residue in the oven produces hard coke.

Commercial Production of Low Temperature Coke is done by :

- Carbonisation in thin layers in externally heated, vertical metal retorts-coalite or parker process.
- Internal heating by heat from the products of combustion of part of the gas yield-Rexco Process.
- Carbonising in continuous vertical gas retorta.



2.1.4 METALLURGICAL COKE PRODUCTION:

Mainly two types of ovens are used for metallurgical coke production. They are:

(a) *Beehive coke oven*

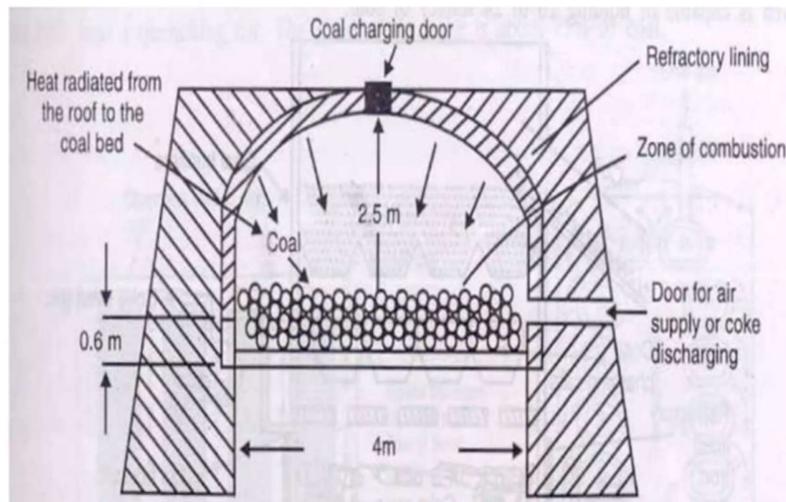
(b) *By-product coke ovens:*

- (i) Waste heat ovens
- (ii) Regenerative ovens.

High Temperature Carbonisation (HTC): It is used for making metallurgical There are two types of coke ovens for HTC namely Beehive oven and by-product oven.

(a) **Beehive Coke Oven:**

- It is made of firebricks with an arched roof having a shape of beehive. There is a circular opening at the top for coal charging and subsequently for exhausting flue gas out of the oven. There is a side door through which the coke is discharged after coking.
- Typical dimensions of a beehive oven are; height 2 metres, base diameter = 3.5 metres, capacity 5.7 tons of coal.



Beehive coke oven

- Heat for carbonisation is supplied by burning of volatile matter of coal and partly by coal itself. Evolved gases burn with the air sucked through an opening at the top of the closed door.
- Carbonization proceeds from top to the bottom of coal charge. At the end of carbonization, the door is opened and the coke is quenched with water and then discharged manually or by machine.

Demerits and merits of beehive oven practice of coke making are given below.

Demerits of Beehive Coke Oven:

- No by-products recovery, is possible.
- Lower coke yield due to partial combustion of coal
- Blends of inferior coal can't produce good coke.
- Lack of flexibility of operation.
- Coke yield is only 60% as against about 77% of dry coal in by-products oven.
- Large coking time. 2-3 days is required for carbonisation. (reduced coke production rate)

Merits of Beehive Coke Oven:

- Strong, blocky coke having good reactivity are produced.
- Low capital and running cost.
- Coke production is not connected with the availability of market for by-products.
- It can be shut down without any damage to refractory unlike by-product ovens,
- Produces hard coke for foundry.

- Simplicity of construction..
- -No extra fuel is required for heating as in by-product oven.

This method of coke making has become obsolete though it is being used in India to some extent.

(b)By product coke ovens:

- It consists of a rectangular refractory chamber of length 15 metres, height 5 metres and width 0.4 metres with removable doors at both ends to enable the hot coke to be pushed out with a ram. The width of the coke discharge side is slightly more (3-4 cm more than the pusher side).
- A large number of ovens with heating flues in between, is arranged in a battery with regenerators for heat exchange between hot flue gases and combustion air, placed below.
- The coking coal blend is usually introduced by several (typically three) top charging holes.
- Each pair of ovens which is separated by a system of vertical flues can be heated by producer gas, coke oven gas, or blast furnace gas or mixed gas.
- Air for combustion is preheated in regenerators Blast furnace gas, mixed gas or producer gas, if used for heating can also be preheated but coke oven gas is not preheated as hydrocarbons (mainly methane) present in it.
- Flue temperature in the heating chamber is maintained at about 1200-1300°C.
- Carbonization time for a 22tons wet coal charge varies from 16 to 18 hours depending upon the width of the oven.
- The oven walls are made up of silica bricks.

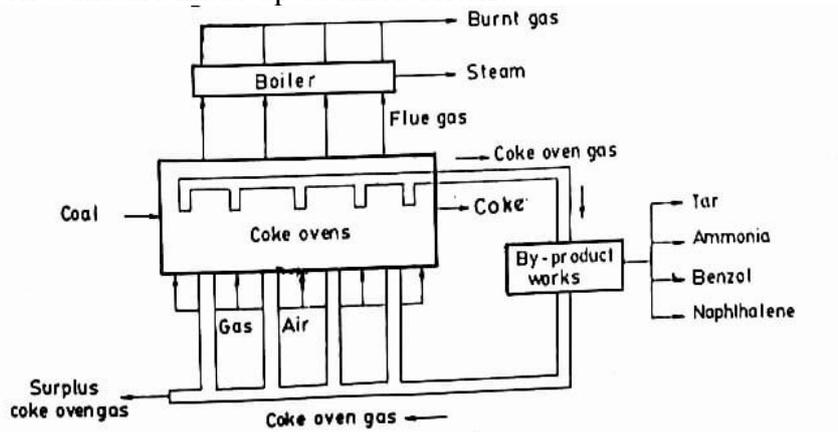


Fig: By product coke oven

2.1.5 Physical And Chemical Properties of Metallurgical Coke.

Ash and moisture content in coke:

- Low moisture and Ash content are desirable in metallurgical coke. Low moisture in coke can be achieved by suitable control of water supply during quenching.
- Metallurgical coke should contain <1.5% moisture.
- Each additional 1% H₂O in blast furnace coke increases fuel consumption by 1.2%.
- Maximum desirable Ash in metallurgical coke is 8-10%.
- Each additional 1% Ash in blast furnace coke increases fuel consumption by 2%
- In addition, high ash content becomes very undesirable if it causes trouble in fusion.
- Volume of slag produced in blast furnace becomes more with the use of high ash coke resulting in reduction of the useful volume of the blast furnace and hence production of pig iron from blast furnace is reduced.
- High ash coke has high resistance to abrasion and has strength.

Density and porosity –

- The more complete the coal is devolatilised the more closely the density of coke approaches that of the graphite.
- Coking follows formation of a porous structure which increases in density by shrinkage during further heating at a high temperature.
- Coke contains traces of hydrogen and matter of the coal.
- Its absolute density never reaches that of graphite
- The higher the rank of the coal the higher is the density of coke made (varies from 1.7 to 1.95 for c% in coal from 81 to 89% .
- Increase in time and temperature of carbonisation (with faster heating rate) the density of the coke increases while the porosity decreases. Having low porosity are strong and harder.

Sources of coke	Bulk density kg/m³ sized (18-40mm)	unsized
Coke oven.	417-480.	465 -513
Horizontal retort	368-417.	400-548
Continuous vertical retort.	337-353.	368
Low temperature retort	305	320

- Porosity of high temperature coke varies from 40-50%.
- High porosity is desirable in future cokes to obtain high rates of combustion.
- In blast furnace high strength is considered.

Hardness and strength –

-It is defined as the resistance power of material to breakage by Impact.

- Strength of coke is measured by 'shatter index' while its hardness is measured by Cochrane abrasion index.
- Hardness and strength of coke are measured by a parameter micum index.
- Sundgren drum test is used to determine the coke strength and hardness

Shatter Index:-

- It measures the resistance of coke to breakage by Impact.
- Its Strength 50 lb or 20 Inches Size Cake is placed in a rectangular box of dimension 8 inch × 18 Inch × 15 Inch placed 6 ft above a steel base plate half inch thick.
- The hinged base of the box is released suddenly when the Content drop onto the base plate.
- Box is dropped Several times and Cake is then screened through a series of sieves.
- The percentage of cake retained on 2inch 15 Inch and 0.5 Inch Sieve, Sieves are recorded and *called shatter Index*.
- Desirable values of shatter Index coke are 80% on 2 inch Screen, 20% on 15 inch screen and 97% on 0.5 screen,

Cochrane Abrasion Index of Coke:-

- It is measure of the hardness of the Coke.
- To Find out abrasion Index, 28lb of 3 inch coke is rotated In a welded steel drum (18 Inch dia. fitted with 2.5 Inch angle iron lifting plates at 17° to axis) at 18 r.p.m For 1000 revolutions.
- The coke is then taken out and sieved through a screen of 1/8 Inch size.
- A high abrasion Index means a high resistance to abrasion.
- Abrasion Index for Blast Furnace Coke should be about 80.
- Abrasion Index Increases roughly by 1% for Increase of 0.2 % in the 1.5 Inch shatter Index.

Micum Index of Coke :-

- This is a measure of both hardness and strength of the Coke.
- 50 kg of Coke of 50 mm Size is rotated in the micum drum for 4 minutes at the rate of 25 rotation per minute.
- After rotating the Coke, It is taken out and screened through 60 mm, 40 mm and

some and 10 mm round hole screen.

- The percentage of coke retained on 40 mm screens called *M40 Index*.
- The percentage of coke that passes through a 10 mm Screen is called *M10 Index*.
- M10 gives the resistance of the Coke to breakage by abrasion and it is a measure of hardness of the coke.
- High M10 and Low M10 values are desirable for metallurgical Coke.
- As per ISI, minimum M40 index should be 75% and maximum M10 index should be 14% for Metallurgical Coke.

Reactivity of Coke :-

- The ability of coke to react with O₂, CO₂ or steam (H₂O).
- Coke of high reactivity ignites easily and gives rapid pick up of fuel bed temperature.
- Low reactivity coke gives a higher fuel bed temp" than a highly reactive coke.
- Reactivity is Inversely proportional to the absolute density.
- Coke of high reactivity are obtained from weakly Caking Coals or blends.
- Strongly Coking, high rank coals produce coke with low reactivity.
- Reactivity of coke is measured by critical air blast method and is reported as critical air blast (CAB) value of Coke.
- Another modern and Current method of expressing the reactivity and strength of coke is *coke reactivity Index (CRI)* and *Coke strength After Reaction (CSR)*

Coke Reactivity Index (CRI):-

- To determine CRI 200 gm of Coke Sample (Size +20-25 mm) is taken in a stainless steel tube and heated in electric Furnace to 110°C.
- Carbon of Coke reacts with CO₂ (depending upon the reactivity level of the coke) and there is a loss of weight of coke depending upon its reactivity.
- More is the loss in weight of the Coke, reactivity is more.
- % loss in weight of cake is reported as Cake Reactivity Index (CRI).
- Ideal CRI value of a good blast furnace coke should be about 20%.

Coke strength after reaction (CSR)

- The left out coke from the CRI determination test is rotated for co-rotation in a micum drum.
- And the % of coke retained on a 10mm size screen is reported as coke strength after reaction(CSR).
- Stronger the coke more is its CSR value. Ideal value of CSR for blast furnace coke is minimum about 55%.
- Typically CSR of Indian blast furnace coke is about 60-65.

Phosphorous & sulphur content

- Coke used for making pig iron by acid process. (i.e. furnace with acidic brick) should have phosphorous <0.012% as phosphorous can not be

removed by the lining .

- Phosphorous present in coke cold shortness in the steel produced where as sulphur cause hotshortness of steel during rolling.
- Sulphur in coke become part of the metallurgical load metal and slag.
- Iron marking 90% sulphur comes from coke and most of it should be removed as calcium sulphide rencesstitating an addition of limestone and corresponding amount of coke to heat and melt it.

Typical specification for india metallurgical coke –

Ash =20-25% minimum.

True density =1750 – 2000 kg/ m³

Abrasion index =77-82%

S = <0.7%

P = < 0.2%

Moisture = 4.5%

Volatile matter =2%

Porosity = 35 – 45%

Bulk density = 420 – 480 kg / m³

Micum index: M₄₀ > 78% and M₁₀ < 10%

Shatter index: 1.5¹¹ index = 85% and 0.5¹¹index = 97%

Caking index of coal blend used for carbonization = 21- 22,

CRI = 20

CSR = 65

3.0 LIQUID FUEL

Petroleum is a naturally occurring brown to black oil comprising mainly hydrocarbon found under the crust of earth.

It obtained from the ground either by natural seepage by drilling wells to various depth. Either petroleum oil flows out itself due to underground gas pressure or these are mechanically pumped out.

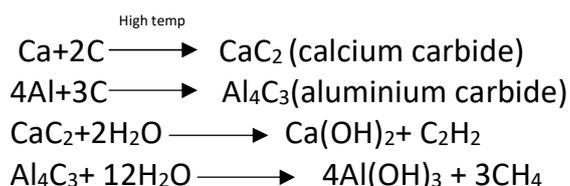
3.1.1 Origin of petroleum:

Although several theories were put forward to explain the formation of petroleum, only three widely accepted ones are given below.

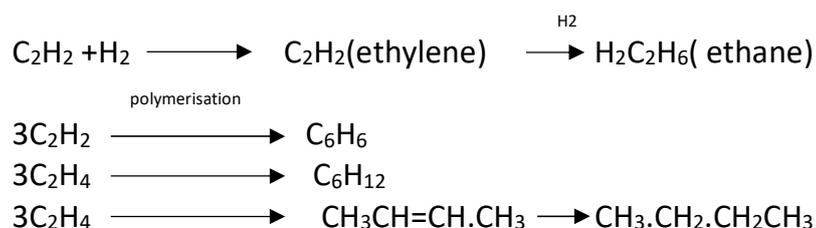
1) Carbide theory:

According to this theory, hydrocarbons present in petroleum are formed by the action of water on inorganic carbides.

In organic carbides, in turn, are formed by the reaction of metal and carbon under high temperature & pressure conditions inside the earth.



These lower hydrocarbons then hydrogenation and polymerization to give various types of hydrocarbons (paraffins, aromatic and cycloparaffins)



However, this theory fails to explain the following facts:

- presence of nitrogen and sulphur compounds.
- Presence of chlorophyll and haemin.
- Presence of optically active compounds.

2) Engler theory:

According to Engler, petroleum is of animal origin. Engler (1900) suggested that petroleum is formed by the decay and decomposition of marine animals under high pressure and temperature. The sulphur dioxide gas given out by the volcanoes beside the sea-side kills the fish and other sea animals which go on piling beside the volcano. After hundreds of years, these animals start decomposing under the influence of high pressure and temperature to form petroleum.

However, this theory fails to account for the presence of chlorophyll (green-colouring matter of plants) in petroleum. Moreover, it does not explain the presence of coal deposits in the vicinity of the oil fields.

3) Modern theory:

- According to modern views, petroleum is believed to be formed by the decay and decomposition of marine animals as well as that of vegetable organisms of the prehistoric forests, i.e. it is of animal as well as of plant origin.
- It is thought that due to some upheavals or earthquakes, these prehistoric forests, and sea animals got buried under the crust of earth.
- Due to action of prolonged action of high temperature and high pressure in the interior of earth for ages, the biological matter decomposed into petroleum.

This modern theory explains the presence of brine and coal in the vicinity of petroleum. Presence of brine is explained on the basis of animal origin while the presence of coal is explained by plant origin.

It also explains the presence of N and S compounds, chlorophyll and optically active compound.

Difference Between Origins of Petroleum Oil and Coal:

Petroleum oil was formed mainly from sea plants and animals decaying under strongly reducing conditions while the coal was formed mainly from land plants decaying under mildly reducing conditions.

Coal seams remained static where formed/deposited while oil can migrate under the effect of pressure and temperature.

Composition of Petroleum:

A typical composition (by weight %) of petroleum is given below:

Carbon=84-87%

Nitrogen=0.1-1.5%

Hydrogen= 11-15%

Sulphur= 0.1-3%

Oxygen 0.3-1.8%

3.1.2 Typical properties of crude oil:

Specific gravity= 0.80-0.95, viscosity at 37.8°C = 2.3-23, cst carbon/hydrogen ratio= 6-8, pour point=18-30 °C, wax content = 6-12%, flash point = 15 - 27°C water content = 0.1-1.5, Salt content = 1.5-8%, Ash content = 0.004-0.006%.

CLASSIFICATION OF PETROLEUM

Depending on the nature of hydrocarbons present in it, crude petroleum oil is classified as:

- paraffinic crude oil (residue left on distillation is paraffin wax)
- naphthenic crude oil (residue left on distillation contains asphalt plus little of paraffin wax)
- asphaltic (aromatic) crude oil (residue on distillation contains asphaltic materials)
- mixed crude oil (containing all paraffinic, naphthenic, and aromatic constituents)

Indian crudes are mostly mixed crude oil. Naharkatia (Assam) crude contains 40% paraffins, 25% naphthenes and 35% aromatics.

Paraffins having general formula C_nH_{2n+2} are saturated hydrocarbons (where $n = 1$ to 35) e.g. methane (CH_4), propane (C_3H_8), pentane (C_5H_{12}) etc.

Naphthenes having general formula C_nH_{2n} are saturated ring compounds (where $n = 1$ to 9) e.g. C_4H_8 , (cyclo-butane), C_6H_{12} (Cyclohexane) etc.

Aromatics having general formula C_nH_{2n-6} ($n \geq 6$) contain 6 carbon atoms in the form of a hexagon shaped ring and are unsaturated ring compounds e.g. benzene (C_6H_6), toluene($C_6H_5CH_3$), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$).

3.1.3 REFINING OF PETROLEUM

The process of dividing petroleum into fractions with different boiling range volatilities and free from impurities is called refining.

Petroleum is refined by *fractional distillation* process.

Fractional distillation: The process of condensation and vaporisation takes place many times causing separation of the constituents of petroleum according to their boiling points.

Operation: Generally crude oil contains compounds having boiling points upto $400^\circ C$. In this process crude oil is heated to above $400^\circ C$ in a furnace. Its vapors are passed through a tall cylindrical fractionating tower column which has a number of plates(compartment) inside it to collect different volatilities.

As the petroleum vapor moves upward, the higher boiling point fractions condense and fall back and only lower boiling point vapors move to higher plates where further condensation takes place and some more liquid falls back. As the freshly condensed liquid comes to the lower plates it gets heated and vaporised and again condenses on higher plates. This process of condensation and vaporisation takes place many times causing separation of the constituents of petroleum according to their boiling points. Thus, the higher boiling point fractions condense towards the lower part of the column and the lower boiling point fractions towards the upper part.

Normally, all the crude is not distilled at atmospheric pressure, otherwise the higher boiling hydrocarbons will thermally decompose (crack). The unvaporised crude oil removed from the bottom is distilled under vacuum at lower temperature to get higher boiling point products.

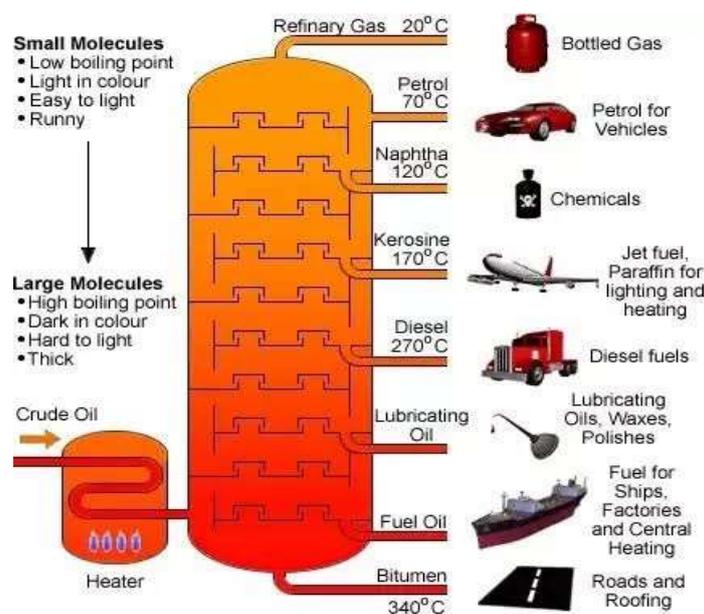
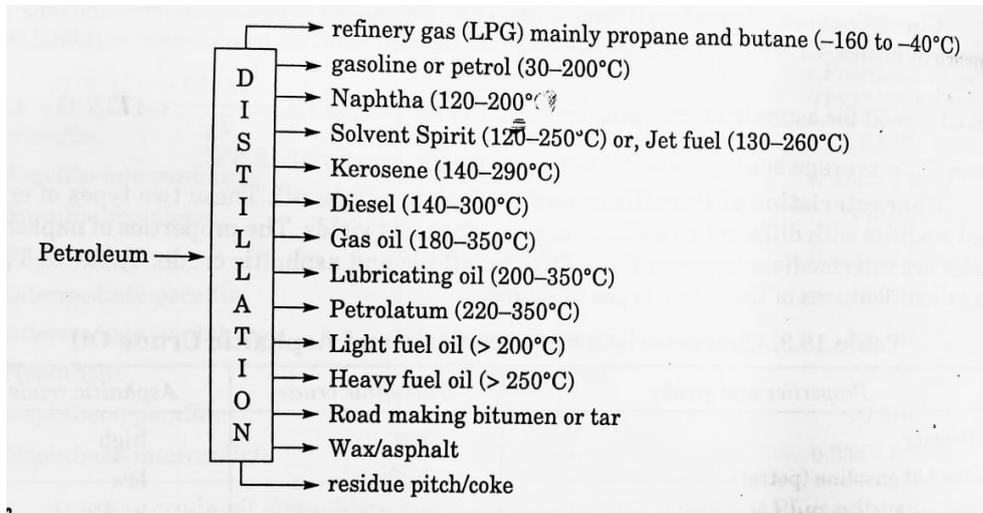


Fig: Fractional distillation of petroleum

USES OF PETROLEUM PRODUCTS:-



[Fig: products of petroleum]

- *Liquefied Petroleum Gas (LPG)*- Domestic and industrial fuel. It is also called refinery gas. It is liquefied before use. It is mainly a **mixture of propane and butane**.
- *Gasoline (Petrol)*-Fuel for spark ignition internal combustion engine (motor/aviation), dry cleaning of clothes.
- *Naphtha* - Used as solvent, paint thinner, blending of motor fuel. Its most important use is in the production of H_2 (used in making nitrogenous fertiliser) by its steam reforming. It is used as a fuel gas (naphtha vapor) in steel plants.
- *Jet Fuel*-Fuel for jet plane, aviation turbine engines.
- *Kerosene* - Domestic illuminant and tractor fuel.
- *Diesel*-Fuel for diesel engines. (compression ignition engine)
- *Gas oil*-It is gasified for fuel gas production. It is a fuel for industrial furnace. It is also used as blend for heavy fuel oil.
- *Lubricating oils* - Used as a lubricant in machines and engines.
- *Petrolatum* - It is also a lubricant used as a base material for grease manufacture.
- *Light fuel oil*-Used as a fuel in industrial furnaces.
- *Heavy fuel oil* - Used as furnace fuel after blending with light fuel oil or naphtha to reduce its viscosity and improve fluidity and atomisation characteristics. It is also

- cracked to produce gasoline, diesel, gas, light fuel oil etc.
- *Bitumen or Tar*- Used for road making as binder and for moisture proof coating.
- *Wax* - It is used for making candles, waxed papers and cartons, match stick coating. Rust prevention etc.
- *Residue Pitch* - For making road and as industrial fuel and electrodes.

Typical Products Yields in Crude oil Distillation:

The yield of products of a typical crude oil distillation is given below (volume percent):

PETROL=18%

Gas oil (fuel oil)= 12%

Naphtha = 6%

Lubricating oil = 12%

Kerosene=10%

Wax=9%

Residue pitch=25%

This yield percentage will widely vary depending on the type of crude and refining operations.

3.1.2 PROPERTIES OF PETROLEUM PRODUCTS:

The important properties of liquid fuels/petroleum/petroleum products that make them suitable for specific uses differ from case to case. No single test or property can evaluate them. Some of the important properties of petroleum products are discussed below.

▪ SPECIFIC GRAVITY

-It determines the maximum power per unit of weight/volume.

-Hydrocarbons of low specific gravity (paraffins) possess the maximum thermal energy per unit volume.

-Hydrocarbons of high specific gravity (aromatics) possess the maximum thermal energy per unit weight).

-Aromatics produce more carbon deposits than paraffins.

-Aromatics have higher Sp. gr. than paraffins.

-Hydrometer is used for determination of specific gravity upto 0.001. For higher values, specific gravity bottle is used. For a semi-solid mass like tar, an indirect method is used.

Specific gravity of tar is given as

$$\rho_T = 2\rho_M - \rho_K$$

where,

ρ_T =specific gravity of tar

ρ_M =specific gravity of mixture of tar and kerosene

ρ_K =specific gravity of kerosene

Specific gravity can be used to find the gross calorific value (GCV) of petroleum products using following formula of U.S. Bureau of Mines.

$$\text{G.C.V.} = 12400 - 2100\rho^2$$

where, ρ = specific gravity of oil at 15.5°C.

-Higher specific gravity means higher carbon to hydrogen ratio.

-Hence, heavier oils have lower gross calorific value on weight basis but higher gross C.V. on volume basis.

-Aromatics have higher specific gravity than paraffins.

-Increase in specific gravity means decrease in paraffin content. An increase in specific gravity increases the amount of heat per unit volume.

▪ ***VISCOSITY***

Viscosity of oil/petrofuels is an important property, because:

- high viscosity fuel oil can not be properly atomised resulting in loss of fuel by way of incomplete combustion.
- highly viscous oil has to be preheated to reduce the viscosity to minimise the pressure drop in pumping to different refineries from the oil field.
- high viscosity lubricating oil reduces its fluidity besides causing undue friction.
- in case of lubricants, it determines the bearing friction, heat generation and rate of flow under particular conditions of load, speed & design.
- it affects the amount of fuel that can be drawn through a wick to a flame by capillary action.
- it affects the flow through pipelines, injector nozzles & orifices.
- it decides the pump clearance; which if out of range, results in pump seizer.

Viscosity is determined by three makes of commercial viscometers.

In case of viscometers, a fixed volume of liquid at a fixed temperature is allowed to flow through a standard capillary tube and the time of flow is noted.

Kinematic viscosity measured by this method is expressed in stokes or centistokes.

▪ ***FLASH POINT & FIRE POINT***

Flash point: It is the minimum temperature at which an oil/petrofuel gives out sufficient vapour to form an inflammable mixture with air and catches-fire momentarily i.e. flashes, when flame is applied.

Fire point: It is the lowest temperature at which vapors given off by oil ignites and continues to burn for at least 5 seconds. In most cases, fire point is 5-40°C higher than flash point and is determined in the same apparatus as for flash point determination.

Flash point & fire point of an oil gives an idea about the:

- nature of boiling point diagram of the system
- amount of low boiling fraction present in the liquid fuel
- explosion hazards during storage and handling
- volatility of the liquid fuels.

3.2.1 Determination of flash point & fire point:

Pensky-Marten's apparatus is used for the determination of flash point above 50°C eg, for fuel oils, lubricating oils, bitumens etc. Abel closed cup apparatus is used for more volatile oils with flash point below 50°C.

In *Pensky-Marten closed cup apparatus* dried oil is filled up in the cup with lid and heated by a burner. Oil is exposed to flame at every 2°F rise in temperature of the oil. The temperature at which the distinct flame first appears inside the cup by applying test flame through the opening.

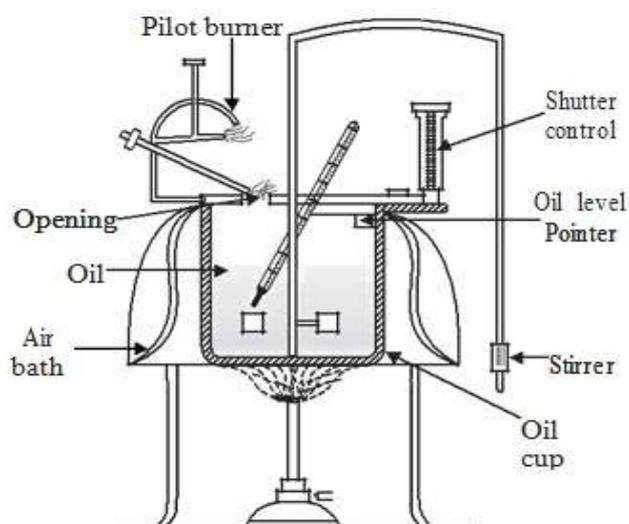


Fig. Pensky Marten's flash point apparatus

-An oil cup of 5 cms diameter and 5.5 cms deep in which oil is filled up to the level marked inside. Four openings of standard sizes are provided in the lid of the cup. Through one of these passes a thermometer and the second opening is used for introducing test flame. Through third opening passes the stirrer carrying two brass blades. Fourth opening is meant for admission of air.

-*Shutter* is a lever mechanism, provided at the top of the cup. By moving the shutter, opening in the lid opens and flame (carried by a flame exposure device) is dipped in to this opening and brings the flame over the oil surface.

- *Flame exposure* device is a small flame and this is connected to the shutter by a lever mechanism.

- *Air bath*. Oil cup is supported by its flange over an air bath, which is heated by a gas burner.

-*Pilot burner*. As the test flame is introduced in the opening, it gets extinguished, but when the test flame is returned to its original position it is automatically lighted by the pilot burner.

Working: Oil under test is filled up to the mark in the oil cup and it is heated by heating the air bath by a burner. Stirrer is worked between tests at a rate of about 1 to 2 revolutions per second. Heat is applied so as to raise the oil temperature by about 5°C per minute. At every 1°C rise of temperature, flame is introduced for a moment by working the shutter. The temperature at which a distinct flash appears inside the cup is recorded as the *flash point*. The

heating is continued thereafter and the test flame is applied as before. When the oil ignites and continues to burn for at least 5 seconds, the temperature reading is recorded as the *fire point* of the oil.

▪ CLOUD POINT, POUR POINT AND FREEZING POINT

These properties are related to the flow conditions of crude oil and its products at low temperature.

Cloud Point: When an oil is cooled at a specified rate, the temperature at which it becomes cloudy or hazy is called the cloud point of oil.

This haziness is due to the separation of crystals of wax or increase of viscosity at low temperature.

It is determined by cold filter plugging point test to find out the extent to which diesel fuel or gas oil will flow even though the temperature is below which the wax crystal will appear i.e., cloud point.

Cloud point is important for fuel oils which have to pass through unheated filters of fine mesh e.g:-a jet plane may be exposed to -60°C and if solid wax separates from fuel oil, the carburettor may be blocked up.

Pour Point: The temperature at which the oil just ceases to flow (or pour) is called the pour point.

It determines the temperature below which, an oil can not be used as a lubricant as well as the waxy nature of oil.

To determine the pour point, the oil is cooled in the test jar and with every 3°C fall in temperature tilted to observe the flow of oil. The temperature at which it does not flow even when kept horizontal for 5 seconds is taken as the pour point.

Naphthenes and aromatics have lower pour point than paraffins.

Determination of pour point is carried out with the help of *pour-point apparatus* shown in fig.

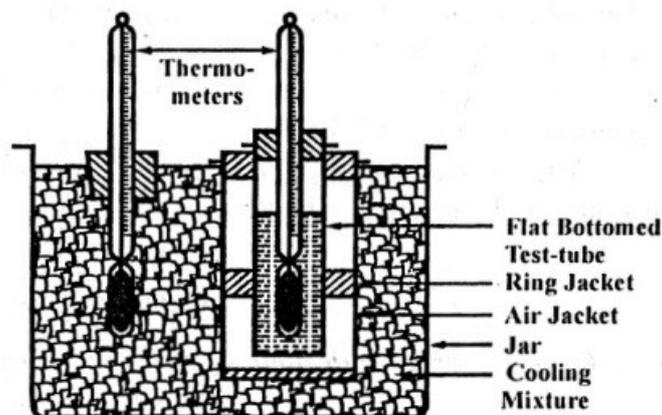


Fig. Pour Point Apparatus

Cloud point and pour point indicate the suitability of lubricants in cold conditions. *The difference of pour point and cloud point is 4-6°F usually.*

Freezing point: It is the temperature at which the fuel oil freezes completely and can not flow at all.

This is important in case of aviation gasoline because at high altitudes where low temperatures are encountered, the fuel supply from fuel tank to engine may be impeded due to choking of pipeline if the freezing point of the fuel oil is not sufficiently low.

Paraffins possess higher freezing points than naphthenes and aromatics.

▪ SMOKE POINT AND CHAR VALUE

These properties of *kerosene* determine the suitability of kerosene as a fuel and as an illuminant.

Smoke point: This is the maximum height of flame in mm without smoke formation when the kerosene is burned in a standard lamp under closely controlled conditions.

To determine, smoke point, kerosene sample is burned in a standard lamp with a specified wick for five minutes and the height of flame is read when it leaves no smoky tail.

A good quality kerosene used for domestic use should have high smoke point (about 25mm).

Char value: It is the amount of charred oil deposition on the wick obtained from Kerosene after burning in a standard wick lamp at a standard rate for 24 hours.

The weight of char is estimated from that present in the upper portion of the wick after washing with light petroleum spirit and drying at 100-110°C.

Char value should be less than 20 mg/kg of kerosene for a good quality kerosene.

▪ 3.2.2 ANILINE POINT

It is the lowest temperature at which an oil is completely miscible with an equal volume of aniline.

It is the measure of the aromatic content of the oil, hence is a characteristic property of diesel.

For aromatics, aniline point is low and the ignition quality is poor.

Hence, higher the aniline point, better the diesel fuel and the lubricant.

▪ OCTANE NUMBER



-This is a property of *gasoline* which is used in a spark ignition engine and expresses its knocking characteristics.

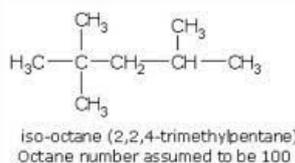
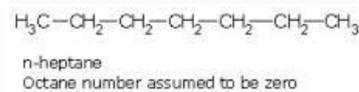
When a gasoline engine is made to operate at high load and low speed, a sort of rattling noise may develop from the combustion chamber resulting from unsteady and uncontrolled combustion. This noise is called *knocking or detonation*.

-Knocking is harmful to engine as its parts are set to vibration there by reducing the life of engine. Knocking depends upon the quality of fuel also.

Octane number requirement of petrol engines depends on their compression ratio.

-It has been found that n-heptane knocks very badly so its anti-knock property has been arbitrarily taken as zero and iso octane (2, 2, 4 trimethyl pentane) gives very little knocking so its anti-knock value has been taken as 100.

Octane number of the fuel is defined as "the percentage by volume of iso-octane in a mixture of n-heptane and iso-octane with the same knocking tendency as fuel". Thus if a sample of gasoline gives as much knocking as a mixture of 80 parts of iso-octane and 20 parts of n-heptane, its octane number is 80.



-Higher the octane number, better is the fuel as maximum permissible power increases with the octane number besides causing minimum knocking.

-Octane number of hydrocarbon fuels increases in the order n-paraffins- olefins-naphthenes-iso-paraffins-aromatics.

-To determine the octane number of a fuel, it is burnt in a standard engine and the knock is measured by a *knockmeter*.

-In India, motor gasoline of octane number 87 is sold whereas the same of aviation gasoline is more than 100. In USA, octane number of standard and premier gasoline is 94 and 100 respectively.

-Octane number of gasoline is improved by the addition of tetra ethyl lead (TEL).

TEL is a very good anti-knocking agent. Constituents of gasoline respond differently to the addition of TEL This is called lead response and decreases in the order paraffins-naphthenes - olefins- aromatics. Alcohols respond negatively as do sulphur compounds.

▪ CETANE NUMBER

It is a characteristic property of *diesel* and is used to indicate its quality and performance in compression ignition engine.

In case of diesel engine, the fuel should ignite as soon as it is injected into the cylinder. If it does not ignite instantaneously, (the time lag between fuel injection and fuel ignition is called *ignition delay period*) abnormal combustion takes place resulting in shock waves, due to fluctuating pressure rise in the cylinder. With diesel of long ignition delay period, much of the charge is injected into the cylinder before ignition is initiated, causing violent combustion, sudden increase in pressure and rough and bumpy running. This is called *diesel knock*.

Cetane ($\text{C}_{16}\text{H}_{34}$) has a very small ignition delay period hence it is given a cetane number rating of 100 a-methyl naphthalene has a very high ignition delay period, hence it is given a rating of zero.

Cetane number of diesel oil is the percentage by volume of cetane in a cetane/a-methyl naphthalene mixture that has the same ignition delay period and performance in a standard compression ignition engine as that of the fuel.

Diesel oils for high speed (> 1500 rpm), medium speed and low speed engine should have cetane number not less than 50, 35 and 20 respectively.

Cetane number increases in the order aromatics - iso-paraffins-naphthene-olefins-n-paraffins, whereas the octane number decreases in the same order.

The result is that a oil of high cetane number has a low octane number and vice-versa. A petroleum crude which gives diesel oil of high cetane number, gives gasoline of low octane number. A good spark ignition fuel makes a poor compression ignition fuel and vice-versa.

1-1.5% of additives called "dopes" like ethyl nitrate, acetone, iso-amyl nitrate etc. are added to improve the cetane number. Cetane number is determined by a standard test compression- ignition engine by measuring the ignition delay.

High cetane number diesel fuel will facilitate easy starting of C.I. engines particularly in cold weather, faster engine warm up, increased engine efficiency & power output and reduced exhaust smoke, odour & combustion noise.

▪ **EMULSIFICATION**

Some oils mix intimately with water and the mixture is called emulsion which has the tendency to collect dirt, grit, particles and other foreign matters.

▪ **OXIDATION STABILITY**

Oils tends to oxidise in contact with air rapidly at higher temperature.

A common test for it is the Sligh oxidation test in which 10 gm sample of oil is heated in a flask containing pure oxygen at 200°C for 2.5 hours. The flask is cooled, the contents are diluted with naphtha and allowed to stand for an hour. The precipitate is filtered, washed, dried and weighed. The weight is expressed as percentage of the weight of the sample and multiplied by 100 to give Sligh oxidation number.

▪ **ACID VALUE/NUMBER**

Acid value or number determines the acidity of an oil. It is defined as the number of milligrams of the KOH required to neutralise the free acid present in 1 gm of oil.

▪ **COLOUR AND FLUORESCENCE**

Colour of petroleum products indicates the degree of refinement. Distillates are lighter in colour than the residual oils. A pale colour does not indicate lower viscosity.

The mineral oils show fluorescence in reflected light whereas fixed oils do not show fluorescence. Hence fluorescence helps to detect adulteration.

▪ **SULPHUR CONTENT**

Even after purification, petroleum products do contain some or other quantity of sulphur. Sulphur content increases with the increase in the boiling range of the products.

Some typical sulphur content values are, Kerosene = 0.05 to 0.2%, gas oil/diesel oil = 0.3 to 1.5% and fuel oil = 2 to 4% (LSHS = 1%)

▪ **MOISTURE**

Water solubility in oil is very low (0.005 to 0.05%) However, it is present in fuel oil upto 1% in dispersed state.

Undesirable water is separated from oil by preheating *Dean and Stark* method is used for its determination in which oil sample is heated with xylene which forms an azeotrope with water.

The distilled vapor on condensation and settling gives water as a separate layer which is measured.

▪ **CALORIFIC VALUE (C.V.)**

Gross C.V of petroleum fuels are in the range of 10000 to 11300 kcal/kg, the higher figure being for gasolines and lower for heavy fuel oils.

Petroleum products are high in hydrogen content (11.8-14.5%) and hence their net calorific value is less than the gross by 620-760 kcal/kg. C.V. of oil is determined in a bomb calorimeter.

▪ **ASH IN PETROLEUM PRODUCTS**

Ash in petroleum products can result from oil, water soluble metallic compounds or extraneous solids such as dirt & rust.

An idea of the ash forming material present in oil can give information about its suitability for use in a given application.

This method describes a procedure for determining the ash content in distillate, residual fuel oils, crude oils, lubricating oils, waxes, and other petroleum products.

3.1.4 Coal Tar Fuels (C.T.F.)

TAR:

Coal tar is a black to brown oily and viscous fluid of characteristic odour produced during high or low temperature carbonisation of coal during coke manufacture.

Tar produced during low temperature carbonisation of coal (700°C) is called low temperature tar whereas, that produced during high temperature carbonisation (at 1100°C) is called high temperature tar.

Tar usually means high temperature tar. Specific heat of tar is 0.3-0.4 kcal/kg °C at 40°C.

Low temperature tar: Its yield is about 10% of dry coal. It is a brown colour oily liquid having very low viscosity, hence flows readily. It is paraffinic in nature. Its typical analysis is C=84%, H=8%, S 0.5%, N = 1%, O= 6.5%.

It contains very less free carbon (3%). It is free from naphthalene.

High temperature tar: It is a thick, high viscosity, black coloured liquid with an aromatic nature. It contains more amount of useful aromatics like phenol, naphthalene, creosote,



Fig: Coal Tar

anthracene, benzol, pyridine etc. Its free carbon content is high (5-180%) and the yield is lower (3% of dry coal). Specific gravity is more (1.18) compared to low temperature tar (1.06).

Difference between low temperature tar and high temperature tar:

<i>Low temperature tar (L.T. tar)</i>	<i>High temperature tar(H.T. Tar)</i>
a) It is produced during low temperature carbonisation of coal at 700°C and is also called primary tar.	a) It is produced during high temperature carbonisation of coal at 1100°C and is also called primary tar.
b) Its free carbon content is practically nil (0 to 1%). Tar yield is higher, about 10% of dry coal carbonised.	b) Its free carbon content is high (5-8%), Tar yield is lower, about 3% of dry coal carbonised.
c) Its specific gravity is lower (1.02 to 1.06).	c) Its specific gravity is higher (1.10 to 1.15).
d) Its viscosity is less, hence it has a better fluidity.	d) Its viscosity is comparatively higher, hence it has poorer fluidity.
e) It is mostly paraffinic in nature having little aromatics.	e) It is mostly aromatic in nature.
f) It contains very little of naphthalene and anthracene (<1%).	f) It contains higher amount of naphthalene & anthracene (about 5%).
g) It has a higher content of tar acids (upto 35%) having higher molecular weight than the tar acids of high temperature tar.	g) It has a very low content of tar acids (3%).
h) Pitch yield on distillation is lower (35%).	h) Pitch yield is higher (65%).
i) It is a raw material for the production of motor spirit and diesel fuel via catalytic hydrogenation. It has a low market value.	i) It has a high market value as it is a source of production of valuable aromatic chemicals like benzol, phenol, naphthalene, anthracene, creosote oil etc.
j) Typical composition (weight%) in various distillation range is as follows: 0-170°C= 6%, 170-230°C= 16%, 230-270°C= 12%, 270°C, pitch= 31%, hard pitch =35%	j) Typical composition is as follows: 0-170°C =2%, 170-230°C= 7%, 230-270°C= 12%, 270°C pitch=14%, hard pitch=65%.

Recovery of tar :

During the carbonisation of coal in by-product coke oven, the tar vapors present in the coke oven gas are separated by cooling it by ammoniacal liquor resulting in its condensation. Remaining tar is separated in primary cooler and electrostatic tar precipitator thereby recovering the bulk of the tar present in the coke oven gas.

Distillation of tar : Tar contains around 300 identified chemicals Hence to recover some of these chemicals economically and to produce better fuel, tar is distilled. The main fractions of tar (which are recovered by distillation), their constituents, yield and boiling ranges.

Uses of tar : Tar is used as a furnace fuel. Its calorific value may be 8500 kcal/kg. Use of crude tar as a fuel possesses a number of disadvantages viz.

- the presence of volatile component which are lost on storage and which increase the fire hazard.
- the presence of water in tar which reduces the calorific value, causes corrosion and its irregular combustion.
- the presence of solid impurities such as coke dust which may choke the burners and pipelines.

Besides, the fact that (tar) is a 'storehouse of chemicals' (its direct use as a fuel) is discouraged. Coal tar is also used as a binder for coal briquettes and for road making purposes.

Coal Tar Fuels (C.T.F.): Coal tar fuels (C.T.F.) are the liquid fuels obtained by mixing the different tar distillation products (fractions). Though the different products of tar distillation contain valuable chemicals, the demand for them is limited, hence large parts of tar is prepared into a series of coal tar fuels.

Six types of C.T.F. are prepared and designated as:

- (a) CTF 50
- (b) CTF 100
- (c) CTF 200
- (d) CTF 250
- (e) CTF 300
- (f) CTF 400

The number indicates the temperature in °F to which the fuel (CTF) should be preheated to reduce its viscosity (upto maximum 25 centistokes) so as to make it suitable for atomisation through burner.

For example, CTF 200 is the fuel which should be preheated at 200°F to decrease its viscosity for smooth atomisation.

CTF 50 does not need any preheating. CTF 50 and CTF 100 are the mixture of carbolic oil, creosote oil and anthracene oil fractions of tar CTF 200, CTF 250 and CTF 300 are the mixture of creosote oil, anthracene oil and residual pitch.

CTF 400 is nothing but residual medium soft pitch having a softening point of 75-80°C. This pitch can be pulverised and used as a pulverised fuel in the furnace. Pitch is also used for coating of roof and pipeline for guarding against corrosion.

Normally, carbon content increases and hydrogen & oxygen content decreases in the series CTF 50 to 400. C/H ratio increases from 11 to 16.5 in this series.

3.1.4 Uses of CTF: Because of low sulphur content and high flame emissivity, it is one of the ideal fuels for metallurgical furnaces. Besides, it is used for power generation, rotary kilns in calcination & cement units and glass melting furnaces.

4.0 GASEOUS FUEL

Gaseous fuels are those which are burnt in gaseous state in air or oxygen to give heat for utilisation in domestic/commercial sector.

A remarkable feature of gaseous fuels is the absence of mineral impurities, consistency in quality and convenience and efficiency in use. On industrial scale, a gas handling system is the least costly of all the fuels.

Some important gaseous fuels are as mentioned below:

- (a) Methane from coal mines i.e. CBM-coal bed methane
- (b) Wood Gas
- (c) Gobar Gas
- (d) Sewage Gas
- (e) Gas from underground gasification of coal
- (f) Natural Gas
- (g) Liquefied Petroleum Gas (LPG)
- (h) Refinery Gas
- (i) Producer Gas
- (j) Water gas and Carburetted Water Gas
- (k) Blast Furnace Gas
- (l) Coke Oven Gas
- (m) LD. Converter (or BOF) Gas
- (n) Coal Gas from Coal Gasification Processes
- (o) Oil Gas from Oil Gasification Processes.

Two more important fuels namely hydrogen and acetylene find wide use in metal cutting, welding etc.

Gaseous fuels are termed as *rich gas* (if calorific value is $> 4000 \text{ kcal/Nm}^3$) and *lean gas* (if C.V. is $< 1500 \text{ kcal/ Nm}^3$).

Hydrocarbon gases and coal gas are example of rich gas, while blast furnace gas and producer gas are example of lean gas.

The classification of gaseous fuel does not solely depend on the calorific value of gas. Both the calorific value (CV) and specific gravity (Sp. gr.) of a gaseous fuel determine the thermal output of a heating appliance.

These two factors are combined to give a CV dimensional group, called Wobbe number or **Wobbe index which is $\frac{CV}{\sqrt{sp.gr}}$** .

METHANE FROM COAL BED/MINES (CBM):

- Methane is associated with coal in mines as it (coal) adsorbs the methane formed-during coalification process.
- At the time of coal mining, the gas is gradually desorbed and it must be removed by proper ventilation otherwise it forms explosive gas-air mixture.
- It is a source of dangerous explosion in gassy mines and the gas is often called as 'firedamp'.
- The methane rich gas from coal mines may be recovered through a system of

boreholes and may be used as a fuel. Methane rich mine gas have been recovered in U.K., France, Germany but the recovery process has not been developed on a wide scale due to availability of natural gas on a large scale.

- The composition of methane gas from coal mines is variable but it is essentially a high concentration methane gas as shown below.

$\text{CH}_4 = 93-99\%$ $\text{C}_2\text{H}_6 = 0-3\%$
 $\text{CO}_2 = 0-4\%$ $\text{N}_2 = 2-6\%$

- Hydrogen and rare gases are present in traces. In India, this gas is not being recovered in any coal mine for use as a fuel and this is a potential source of fire in mines under the crust of earth.
- Recently, exploration of coal bed methane (CBM) has been started at *Telgharia near Bokaro Steel city in Jharkhand*.

WOOD GAS:

- Wood gas is obtained either by carbonisation of wood in metal retorts or by gasification of wood. It is a medium calorific value gas not of much commercial interest.
- Wood gas is also produced by gasification of logs, chips etc. in many countries similar to the principle of producer gas generation from coal.
- Gas yield in typical wood gasification process is about $194 \text{ Nm}^3/\text{ton}$ dry wood. Crude methyl alcohol is also recovered (0.5% of dry wood) in gasification. A typical wood gas composition (produced by gasification) is:

$\text{CO}_2 = 6\%$, $\text{CO} = 29\%$, $\text{CH}_4 = 2.5\%$
 $\text{C}_m\text{H}_n = 0.7\%$, $\text{H}_2 = 14.5\%$, $\text{O}_2 = 0.3\%$, $\text{N}_2 = 47\%$
C.V. 1660 kcal/Nm^3 , Sp. gravity = 0.85 (Air = 1)

- About 50% of the wood gas is consumed in gas producer while rest 50% is available for use elsewhere e.g. in thermal power plant. India does not have commercial generation facility for wood gas.

GOBAR GAS:

- Gobar gas is obtained by the fermentation of gobar (dung) in absence of air. Gobar gas (cattle dung) is derived from cattle dung (called 'gobar' in Hindi).
- In a gobar gas plant, fuel value of the dung is extracted while the refuse can still be used as a fertiliser.
- **Operating Principle-** Gobar gas is produced by the fermentation of dung and other organic materials in absence of air. It consists mainly of CH_4 and CO_2 . The extraction of CH_4 does not affect the fertiliser value of the dung. Rather, after the dung is processed in Gobar gas plant, the manure becomes rich in nutrients and odourless. In addition, it becomes free from flies and other sources of infection. Gobar gas burns with a blue flame without smell at an efficiency five times greater than that of burning cowdung cakes. Hence, this plant provides improved fuel and

organic manure from the dung.

- The plant comprises of a digester to ferment cowdung and any other finally chopped -left-over fodder or vegetable efficiently. The digester is covered by a gas holder which collects and diverts the gas produced into the gas pipe at correct pressure.
- Cattle dung and urine is collected and dumped into the mixing tank, where it is mixed with water and fed to the inlet pipe. This slurry, when enters the digester will discharge an equal quantity of ripe slurry through the outlet pipe which is let into the compost pit and covered with the farm sweepings and other organic wastes from the household which is finally used as a fertiliser. Gobar gas plant is shown in Fig. 30.1.

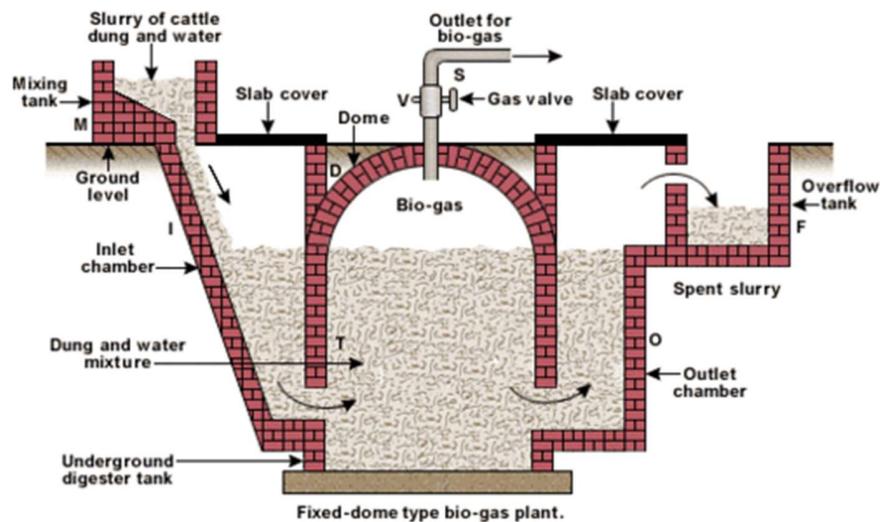


Fig: Gobar gas plant

- **Utilisation of Gobar Gas Plant Products:** Two main products of gobar gas plant are fuel gas and manure.
- **Fuel Gas:** Presence of substantial quantity of methane (55-60%) makes it a very suitable fuel gas.
- **Manure:** The outlet slurry from the plant which is rich in nitrogen (>2%) and humus can be applied directly to the land by mixing with irrigation water.

SEWAGE GAS:

- Sewage gas is produced during sewage disposal by way of anaerobic decomposition of organic wastes (by suitable bacteria). Sewage gas is a methane rich gas which can be used as a town gas component if available in commercial quantity.
- **Composition and Properties of Sewage Gas**

$\text{CH}_4 = 58.5\text{--}76.5\%$, $\text{CO}_2 = 30\text{--}41\%$

$\text{N}_2 = 3\text{--}8\%$, $\text{O}_2 = 0\text{--}1.8\%$

$\text{H}_2 = 0\text{--}4.5\%$, $\text{H}_2\text{S} = 0.1\%$

C.V = 5700-7400 kcal/Nm³ (dry), Sp. gravity = 0.7-0.85, (Air = 1)

Gas yield=8-30 liters per capita of population per day

- Higher HS in sewage gas makes its use difficult in gas engines or boilers without purification.
- Gases similar to sewage gas are produced by fermentation of agricultural wastes (carbonaceous) of plants of animal origin (e.g. straw, fruit peeling etc.) under anaerobic conditions. Residue left after the fermentation of sewage and agricultural waste is a good manure (fertiliser).

COAL GAS FROM UNDERGROUND GASIFICATION OF COAL:

- Coal in the underground mines can be gasified in situ even without mining it out of the crust of the earth. This is termed as underground gasification of coal and the gas thus produced is called coal gas from underground gasification of coal.
- Composition and Properties of coal gas produced by underground gasification of coal:

CO = 10.7%, H₂ = 8.4%, CH₄ = 1.8%, N₂ = 67.4%, CO₂ = 10.5%, C_mH_n = 0.3%, O₂ = 0.9%

C.V = 820 kcal/Nm³ (dry), Sp. gravity = 0.95 (Air = 1).

- Some commercial plants in USSR produce gas by this method for electricity generation. Bituminous, sub-bituminous and mature brown coal deposits are suitable for underground gasification using air and oxygen as gasifying medium.
- India does not have any such commercial gasification system.
- The principle of underground gasification of coal has been shown in the Fig.

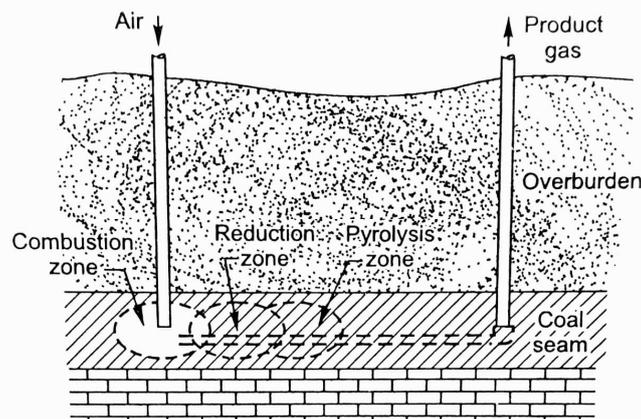


Fig: Principle of underground coal gasification.

NATURAL GAS

- It is a mixture of *paraffinic hydrocarbons*, in which *methane* is the main constituent. It occurs in the gas field (under the crust of earth) and also in association with crude petroleum in oil fields.
- After delivery from wells, natural gas/is processed to remove the solids. It is then treated for recovery of *gasoline and liquified natural gas (LNG)*.
- When natural gas contains very less recoverable condensate ($< 15 \text{ gm/m}^3$), it is known as dry natural gas while it is termed as wet natural gas if recoverable condensate is more ($> 50 \text{ gm/m}^3$).
- This condensate is recovered and is known as *natural gasoline* which is used as a blending agent for motor fuel.
- The condensate (*natural gasoline*) recovery from gas is done by compressing & cooling or adsorption on a porous solid.
- Natural gas of some localities contains large quantity of N_2 and CO plus recoverable amount of helium. Sometimes H_2S are also present in the gas which is recovered as elemental sulphur. (H_2S free gas is called a *sweet gas*).
- Natural gas is used as a fuel for cooking, domestic and industrial heating, process furnace and boilers. It is also used for fertiliser production and as a source of carbon and hydrogen in chemical industries.

Uses of Natural Gas: Natural gas is used for

- Enriching the gaseous fuels of low calorific value e.g. Lurgi gas.
- Internal combustion (I.C.) engine as its high anti-knocking qualities permits use of high compression ratios possible resulting in improved engine efficiency.
- Gas turbines also use natural gas as a fuel.
- Producing carbon black by burning in a limited quantity of air in the presence of cooled metal surfaces. Carbon black is a pigment as well as a reinforcing agent for rubber.
- Making water gas as its methane content can be reacted with steam for this purpose.
- Making synthesis gas (by reaction with steam) which is further used for the production of methyl alcohol or gasoline (by Fischer-Tropsch-process) or hydrogen for ammonia synthesis.
- Partially converting into hydrogen, methane, benzene and other aromatic compounds by pyrolysis which are all valuable chemicals.
- The production of methyl alcohol and formaldehyde by controlled oxidation of methane present in it.
- Producing methyl chloride by the chlorination of methane present in it.

In USA, natural gas is widely used in domestic heating & cooking and a wide network gas pipeline has made it available to almost each and every home. In India natural gas is available from Gujarat, Assam and Bombay high oil wells. A 1700 km long pipeline (HBJ pipeline) running from Hazira to Jagdishpur via Bijapur supplies natural gas to fertiliser

plants and thermal power stations enroute.

Liquefied natural gas (LNG) is shipped also. Oil and Natural Gas Corporation Ltd. in India has set up a bottling plant at Uran (Near Bombay High) for filling LNG in cylinders.

Compressed Natural Gas (CNG): Natural gas has a very low energy density; hence to use it as an alternative fuel for a spark ignition engine on board the vehicle/car, it has to be either compressed to a high pressure of 200 atm or cooled to -160°C to liquefy it for storage.

Hence, it is used as compressed natural gas (CNG).

Advantages of CNG over petrol as a S.I. engine fuel.

- Octane number of CNG is 130, hence it does not need anti knock additive like TEL, which causes pollution.
- Its combustion is more regular and it rapidly disperses into atmosphere at normal pressure and temperature.
- It is a light weight gas with a high ignition temperature and is no more dangerous than petrol.
- Emission of carbon monoxide and unburnt hydrocarbons is comparatively less in the exhaust.
- CNG is insoluble in engine oil, hence lubricating oil retains its properties for longer duration resulting in longer interval between oil changes.
- CNG fired engines have longer life, as it does not carbonise spark plugs or wash out lubricating oil films.
- It has a comparatively better cold starting characteristics, because unlike petrol, it does not first have to be vaporised and it does not condense on cold engine parts.

Disadvantages of CNG:

- CNG storage tanks add weight because heavy cylinders are required for the storage of natural gas at high pressures.
- CNG storage tanks take up five times higher trunk space for comparable energy storage.
- Refuelling station cost of CNG is very high.
- Compared to petrol driven vehicles, CNG driven vehicles have shorter operating range.

LIQUIFIED PETROLEUM GAS (LPG)

- It is mainly a mixture of *propane and butane* used mainly as cooking gas in domestic ovens as well as for industrial heating in furnaces (e.g. heating of annealing furnaces).
- C_3 (propane etc.) and C_4 (butane etc.) hydrocarbons are easily liquified at room temperature with the application of very low pressure.

- Hence, propane and butane is liquified, stored and transported in light cylinders. Generally, a mixture of about 80% butane and 20% propane is used for filling in LPG cylinders (also called bottled gas).
- LPG is prepared from wet natural gas and refinery gases.
- Even pure butane and propane are also liquified and used as fuels.
- LPG is a highly volatile liquid, which expands 247 times its volume as vapor (1 litre Liquid = 247 litres of vapor). It is non-toxic, does not support life and is heavier than air.
- LPG have high calorific value, high specific gravity, high air requirement and low flame speeds.
- *Since, LPG is odorless, hence odorants like mercaptans (50 ppm) or sulphides are added to detect its leakage from cylinders by smell as mercaptans have very pungent smell.*
- The lighter grade LPG commercially available contains 90% propane and 10% butane.
- LPG is a popular domestic fuel because of the fact that a large concentration of thermal energy is contained in a small portable cylinder. LPG is quite popular fuel for industrial heating also where alternative fuel is not available. There are more than 100 LPG bottling plant in the country. It is also used as a fuel in I.C. engine as well as for welding & cutting.
- Propane and butane are also used for enriching the low C.V. gases in a town gas supply system abroad up to limits of permissible specific gravity.
- A mixture of 20% butane and 80% air has a CV of 6136 kcal/ Nm³ and is outside the limit of inflammability of butane in air.
- The amount of air/inert gas added is such that it is well outside the limit of inflammability (explosion limit) of LPG which is about 1.8-8.5% of LPG in LPG/air mixture.
- Density of liquid LPG, which is non-corrosive to steel, copper, copper alloys and aluminium is, half that of water. LPG is slightly toxic & anaesthetic, if inhaled in very high concentration It has no lubricating property and is colorless in either liquid or vapour phase.
- It is used also for welding, cutting, soldering, brazing and portable blow lambs.
- Propane and butane are also used in the production of petrochemicals. LPG being heavier than air has a tendency to settle down while leaking from cylinder. At times methane rich natural gas is also liquified and sold as bottled gas in cylinders. In that case, it is called Liquified Natural Gas (LNG).

For industrial grade LPG (80% butane + 20% propane): -

- C.V. = 29275 kcal/Nm³ (11200 Kcal/Kg)
- Sp gravity=19 (Air = 1),
- Theoretical combustion air requirement = 29 Nm³/Nm³ of LPG

And for domestic grade LPG (70% propane + 30% butane):

- C.V. 25775 kcal/Nm³
- Sp. gravity= 1.65 (Air = 1)
- Theoretical Combustion air requirement = 26 Nm³/Nm³ of LPG

Use of LPG as a S.I. engine fuel: Use of LPG in a *spark ignition engine* offers following *advantages*.

- LPG is readily miscible with air and can burn at leaner air/fuel ratios.
- Being resistant to preignition, it leaves less combustion chamber deposits.
- It has an excellent cold starting & warm up performance and gives lower emission of pollutants like unburnt hydrocarbons & carbon monoxide.
- Its anti-knocking properties are excellent provided large amount of unsaturates are not present in it.

However, LPG suffers from the following *disadvantages*:

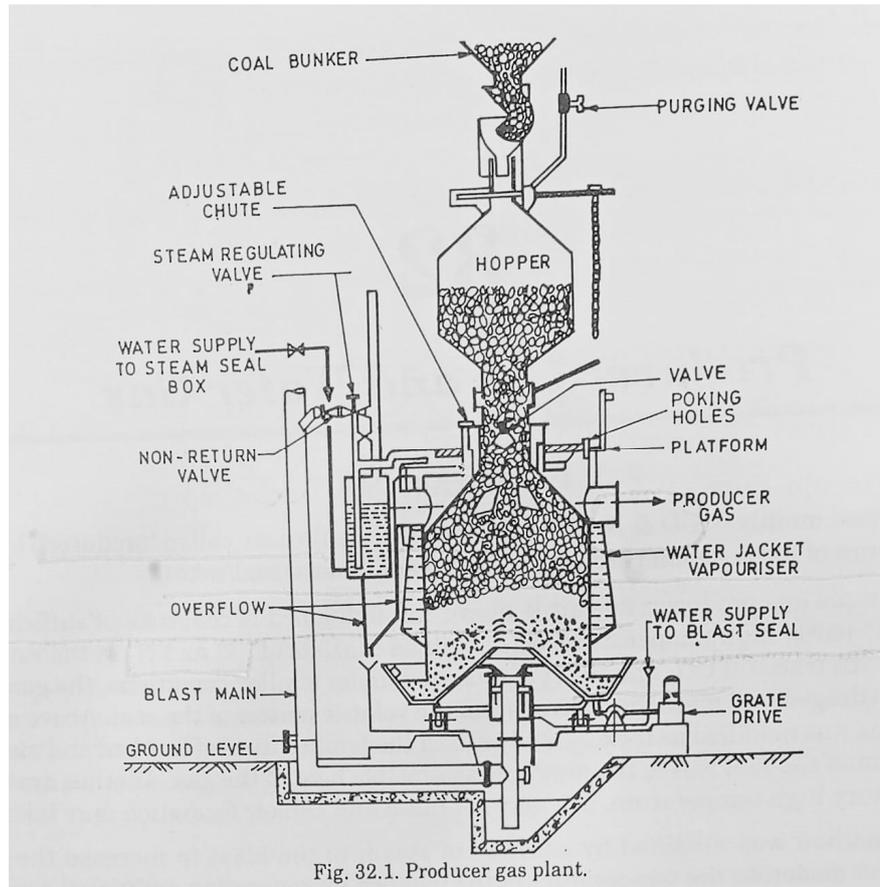
- LPG has to be stored & transported in bulky tanks capable of withstanding very high pressure.
- Some of the unsaturated compounds present in LPG have a comparatively poor octane number and are prone to causing high speed knock.

PRODUCER GAS

- It comprises mainly of CO & N₂ and is produced (in a furnace called 'producer') by blowing air or a mixture of air & steam through hot bed of solid fuels (coal/coke).
- In the simple gas producer, dry air is blown through a bed of coal/coke of sufficient depth and at a sufficiently high temperature. Gas obtained consists of CO and N₂ in the ratio of 1:2 by volume, with traces of CO₂ and H₂.
- Producer gas made from either coke or coal, under normal operating condition has a composition (volume %) within the range given below:
CO₂ = 4-6%, CO = 20-30%, H₂ = 11-20%, CH₄ = 0-3%, N₂ = 46-53%
Calorific value (C.V) = 1250-1550 kcal/Nm³
Sp. Gravity (Air = 1) = 0.85-0.90.

Combustion Air requirement 1-1.3 Nm³/Nm³ of producer gas.

- The producer gas may also contain steam, tarry vapors, sulphur compound, NH₃ in minor quantity.
- The commonest types of gas producer is a vertical cylindrical chamber into which the fuel is fed continuously from the top. Air is blown through a grate at the base, and the gas exit is at the top. Ash and clinker are discharged at the grate. The chamber may be lined with fire brick or may have an annular water jacket in which steam is raised for addition to the blast.
- Principal chemical reactions in producer gas plant using coal/coke as fuel and moist blast (air + steam) for gasification.



USES OF PRODUCER GAS:

- It is used for firing in furnaces (glass melting and steel making in open hearth furnaces), coke oven heating and in internal combustion engines.
- Producer gas for firing in glass melting and open hearth furnaces.
- Producer Gas for Use in Internal Combustion Engines.

🌈 WATER GAS

It is a medium calorific value gas (about 2800 kcal/Nm³) comprising mainly of CO and H₂. It is prepared by action of superheated steam on a bed of hot coke/coal at about 1000 Ca per the reaction

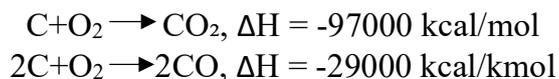


Since the above reaction is endothermic the coal cools down after a few minutes and the reaction proceeds in a different way to form carbon dioxide and hydrogen instead of water gas (CO + H₂).



In order to avoid the above undesirable reaction, the current of steam is intermittently

replaced by a blast of air. The following reactions now occur.



Thus due to exothermic reaction the temperature of carbon again rises and when the temperature increases to 1000°C air entry is stopped and steam is again passed. Thus in modern gas plants steam and air are blown alternatively. The period of steam blow, (cold blow) is usually 4 minutes while the period of air blow (hot blow), is very short about 1-2 min.

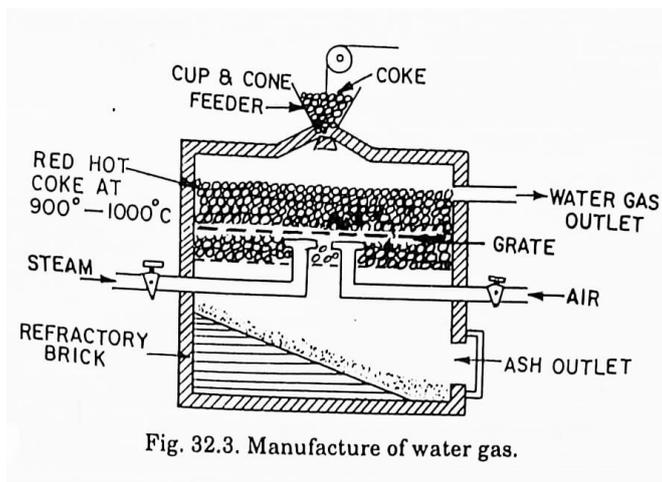


Fig. 32.3. Manufacture of water gas.

During the steam blow, water gas is produced. This is led out through the water gas outlet. On the other hand, nitrogen, carbon dioxide and carbon monoxide are formed during the air blow. These are allowed to escape in the atmosphere. Thus the manufacture of water gas is intermittent.

The best fuel for water gas manufacture is hard cake and anthracite. A typical composition water gas is

$$\text{H}_2 = 48-51\%, \text{CO} = 40-42\%, \text{CH}_4 = 0.1-0.05\%, \text{CO}_2 = 3-5\%, \text{N}_2 = 3-6\%$$

$$\text{Theoretical combustion air requirement} = 2-25 \text{ Nm}^3/\text{Nm}^3$$

$$\text{CV} = 2500-2800 \text{ kcal/Nm}^3$$

$$\text{Sp. gravity (Air=1)} = 0.5-0.55$$

Water gas is also called *blue water gas* or simply *blue gas* as it burns with a bluish flame due to the presence of high quantity of carbon monoxide.

Uses of water gas:

- It is used as a fuel in furnaces.
- Normally, it is enriched by adding hydrocarbon gas (oil gas) and the mixture is *carburetted water gas* which has a high C.V.
- It is also used as a sourer of hydrogen for ammonia synthesis in fertiliser plant.

When water gas is specifically produced for ammonia synthesis, a proportion of air is added to the steam so as to get a mixture of H_2 , CO , CO_2 , and N_2 . This is called *semi water gas*.

✚ CARBURETTED WATER GAS

- CV of water gas is too low for being an effective gaseous fuel in town gas distribution system, However, it can be enriched to make ‘carburetted water gas’ by mixing with hydrocarbon oil vapor having a high C.V. of 10000-13000 kcal/Nm³).
- Process of making carburetted water gas involves both gasification of coal as well as oil and then mixing them (oil gas+ coal gas).
- That means carburetted water gas a mixture of **water gas and oil gas**.
- Carburetted water gas is made by passing water gas through a hot chamber called carburettor into which hydrocarbon oil is sprayed. The oil cracks and produces methane ethane, ethylene, propane and other unsaturated hydrocarbons which have high calorific values.
- The resultant gas mixture is the carburetted water gas with a high C.V. up to 4300 kcal/Nm³. A typical composition and properties of carburetted water gas is given below

$\text{CO}_2 = 5.6\%$, $\text{C}_m\text{H}_n = 7\%$, $\text{O}_2 = 0.4\%$, $\text{CO} = 30.5\%$, $\text{H}_2 = 37.0\%$
 $\text{CH}_4 = 14\%$, $\text{N}_2 = 5.5\%$, Gross C.V. = 4770 kcal/Nm³ dry
 Sp. gravity (Air = 1) = 0.63, Cold gas efficiency = 65% (with light oil)
 Theoretical combustion air requirement = 4.27 Nm³ /Nm³ gas

- The cyclic process of carburetting water gas is synchronised with the parent water gas generation process. And, the resultant gas is passed out of the plant through a wash box.
- Part of the heat produced by blow gas in carburettor and superheater is fed back to the fuel bed by carrying out back run. Steam is blown through superheater and carburettor into the top of the fuel bed. Oil is sprayed into the steam which cracks on passage through the fuel bed. This back-run increases the thermal efficiency of the plant.
- Production of 1 Nm³ of carburetted water gas typically requires steam -0.65 kg, coke-0.45 kg, oil-0.3 kg, air-1.5 Nm³.

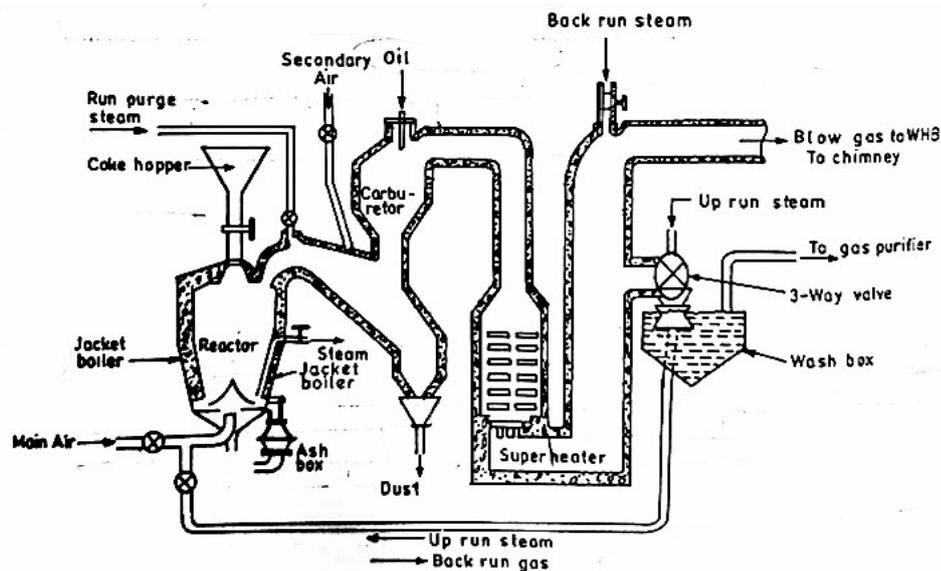


Fig: carburetted water gas plant

- Production of 1 Nm³ of carburetted water gas typically requires steam -0.65 kg, coke-0.45 kg, oil-0.3 kg, air-1.5 Nm³.
- A schematic diagram of carburetted water gas plant is given in above fig. Carburetted water gas is mainly used as an ingredient of town gas and as substitute of coal gas to meet peak loads of gas supply."

BLAST FURNACE GAS

- It is a low grade producer gas made by partial combustion of coke used in the blast furnace and modified by the partial reduction of iron ore.
- It is a by-product of the iron blast furnace. During the manufacture of pig iron, when the air enters the tuyeres, its oxygen reacts with the coke.
- The resulting gas passes up through the shaft of the furnace which has been charged with coke, iron ore, manganese, quartz, limestone, dolomite, sinter etc., and after a number of chemical reactions, issues as a heated dust laden, lean, combustible gas.

Yield of B.F.gas: About 2.5-3 tons of blast furnace gas is generated for one ton of pig iron produced, the coke rate in the furnace being 550-700 kg/ton pig iron. Volumetric is about 1800-2000 Nm³/ton pig iron or about 3000-3200 Nm³ /ton of coke charged in B.F.

Composition of B.F: Gas. A typical range of composition is given below:
CO = 21-23%, H₂ = 4-5%, CO₂ = 18-20%, N₂ = 53-55%, O₂ = 0.2-0.5%

Properties of B.F: Gas. It is a very poisonous gas due to the presence of high amount of carbon monoxide in the gas. B.F. gas pipes and vessels should be leakproof.

Characteristics of B.F. Gas:

- It has a very low calorific value of 800 to 850 kcal/ Nm³, depending upon blast furnace coke consumption rate.
- It has got a low theoretical flame temperature.
- It has a low rate of flame propagation-relatively lower than any other common gaseous fuels.
- It has a high specific gravity (highest of all common gaseous fuels.)
- It burns with a non-luminous blue flame.

Uses of B.F. Gas: Though it has a very low calorific value, yet because of the large quantity of the gas produced, it is one of the most important fuels in an integrated iron and steel plant.

It is used as such or after preheating in:

- Hot dip galvanising line (HDGL) furnace
- Foundry ovens
- Blast Furnace stoves
- Soaking pits
- Annealing furnaces

- Reheating furnace -Billet heating
- Boilers
- Coke oven underfiring

Great care is taken in its utilisation, because of its toxic & poisonous nature and the surplus gas may be stored in gas holders or bled out in the atmosphere after burning it, as the case may be.

COKE OVEN GAS

It is produced during high temperature carbonisation of *coking coal*. It is the most important fuel in an integrated steel plant.

Yield of coke oven gas is 290-300 Nm³ of gas/ton of dry coal Carbonised.

A typical volumetric composition of clean coke oven gas is given below:

CO = 7-8%, H₂ = 58-60%, CH₄ = 23-25%, N₂ = 2-3%, CO₂ = 2-4%, O₂ = 0.5-0.8%, C_mH_n = 2-3%

About 20% of the sulphur in coal is evolved with the distillation products. Much of this remains in the coke oven gas as H.S. Gases high in sulphur content are undesirable for metallurgical purposes as they cause brittleness of surface while rolling the steel after hot scarfing the slabs of steel.

FACTORS AFFECTING THE COMPOSITION OF COKE OVEN GAS:

Composition of coke oven gas varies with the temperature of carbonisation, time Effect of temperature and rank & type of coal.

Effect of temperature: With increase in the temperature of carbonization,

- hydrogen content of the coke oven gas increases because of cracking of hydrocarbon
- methane and other hydrocarbon content of the gas reduces due to their cracking.
- carbon monoxide content of the gas increases because of the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ (carbon is produced from cracking of hydrocarbons).
- yield of the gas increases due to volatalisation and cracking of liquid hydrocarbons (mainly tar).
- calorific value of the gas decreases because of substantially large reduction in hydrocarbon content
-

Effect of time: With increase in the time of carbonisation at a given temperature, the hydrogen and the hydrocarbon content decreases resulting in the greatly reduced calorific value.

Effect of rank of coal: With increasing rank, the proportion of hydrocarbon decreases and the proportion of hydrogen increases e.g. the composition of the gas obtained by carbonising anthracite resembles that obtained in the final stage of carbonisation of bituminous coal and is of the gas rich in hydrogen.

Effect of type of coal: Black durains and cannel coals yield gases containing high proportion of hydrocarbons (particularly unsaturates) of high illuminating value.

Characteristics of Coke Oven Gas:

- Unlike B.F. gas, surplus coke oven gas can be bled into atmosphere without burning as it is not that toxic.
- It burns with a luminous to semi-luminous flame depending upon the degree of mixing of gas and air.
- Its rate of flame propagation is considerably higher than that of natural gas, producer gas and blast furnace gas.
- It has a low specific gravity-lowest of all the pure gaseous fuels used in steel industry.
- It has high theoretical flame temperature-little higher than that of natural gas even.
- Its explosive range is about twice of natural gas.

Uses of Coke Oven Gas:

Coke oven gas has a more extended use than B.F. gas, because of

- relatively low distribution cost due to its low specific gravity, high calorific value and cleanliness,
- its ability to develop extremely high temperature by combustion.
- high heat release rate thereby eliminating excessively large combustion chamber furnaces.

Coke oven gas is used mostly in mixture with B.P. gas in the iron and steel works itself for Blast Furnace Stoves heating Coke Oven heating the following usage:

- Boilers of captive thermal power plant
- Sinter Machine furnace
- Soaking pits, reheating furnaces, annealing furnaces etc.
- Forge furnaces and foundry ovens
- Blast furnace runner and ladle drying
- Calcination kilns

 **MIXED GAS**

- It is a mixture of blast furnace gas and coke oven gas in different ratios to have a gas fuel of a desired calorific value and combustion characteristics.
- There are a number of applications where neither B.F. gas nor coke oven gas, when used alone, develop the desired flame characteristics or temperature level for optimum results. By mixing the two fuels of great variance in characteristics, a more ideal fuel can be obtained free specific applications with specific properties.
- The calorific value and the speed of combustion is very high for coke oven gas and very low for blast furnace gas. The desired speed and calorific value can be attained by the proper proportioning and mixing of the two fuels.

L.D. CONVERTER GAS (BOF GAS)

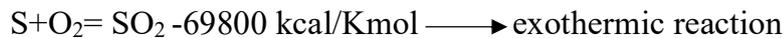
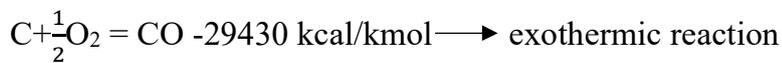
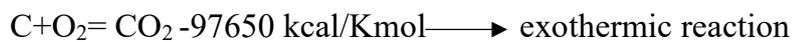
- It is mixture of mainly CO & CO₂, and is produced in L.D. converter during the process of steel making. When oxygen is blown to remove carbon from pig iron in L.D. converter, the converter gas is produced ($C + O_2 = CO_2$, $C+O = CO$).
- The converter gas having a very high concentration of carbon monoxide (up to 80% during peak period) in earlier L.D. converter used to be burnt at the mouth of the converter itself thereby eliminating its toxicity by conversion of CO into CO₂ (viz. $CO + \frac{1}{2} O_2 = CO_2$).
- However, in modern steel making process, the converter gas is recovered as such by suppressing its combustion at the mouth of the converter. It is cooled, cleaned of dust and stored in gas holder for use as a fuel gas.

5.0 Combustion

5.1 Principles of Combustion:

All conventional fossil fuels (solid, liquid or gaseous) contain basically carbon, hydrogen and sulphur which, when burnt react with oxygen of air form carbon dioxide, carbon monoxide, water vapour and sulphur dioxide respectively.

All the fuels contain basic elements such as carbon, hydrogen, sulphur or its compounds. The combustion of fuel is described with the help of few simple chemical equations as given below:



Combustion Process:

In the combustion process the rapid chemical combination of oxygen with the combustible portion of the fuel results in heat release.

The most common fuels contain carbon and hydrogen, either as elements or as parts of compounds. These combustible elements and compounds react with oxygen to form carbon dioxide (CO₂) and water vapour (H₂O). Carbon monoxide (CO) can also be formed. Sulphur is usually present in some fuels.

Combustion on fuel produces *flue gases* which are also called as exit gas, exhaust gas or chimney gas.

The Requirements for Combustion are:

- Fuel
- Oxygen
- The 3T → (a) Time (b) Temperature (c) Turbulence

Fuel: The most commonly used fuels are oil, gas, coal etc.

Oxygen: The normal source of oxygen for combustion is air.

Time: Sufficient time must be available for complete combustion to occur. This time period is significant because of the dilution effect of the nitrogen in the air.

Temperature: When the fuel reaches its ignition temperature, oxidation is greatly accelerated. The fuel/air mixture must be heated to ignition temperature to promote combustion.

Turbulence: It is vital that the fuel and air are thoroughly mixed otherwise complete combustion cannot take place and turbulent mixing is the best approach to this problem.

Generally combustion reaction with an oxidant. Oxygen is the main oxidant. Air is the commonest oxidant because it is cheap and readily available.

Perfect combustion occurs when just enough air has been supplied to burn all the fuel.

By convention, the following analysis are used in combustion calculations:

<i>Air componenets</i>	<i>By volume%</i>	<i>By weight%</i>
O ₂	21	23
N ₂	79	77
Total	100	100

Theoretical air: It is defined as the minimum quantity of air per unit mass of fuel required which is sufficient on combustion to give CO₂, H₂O SO₂ and N₂ as product.

Theoretical air is a fixed quantity for given fuel and is calculated by the stoichiometry/chemical reaction of the variable combustible constituents of fuel.

Excess air: It is the practical amount of air which is supplied in a combustion process usually to ensure that, under the conditions of inadequate mixing of fuel and air, the combustion process is likely to go to completion.

Normally 10, 15-20, 20-25 and 50- 100% excess air is supplied with gaseous, liquid, pulverized fuel and solid lumpy fuels, respectively.

$$\text{Excess air} = \frac{\text{actual air} - \text{theoretical air}}{\text{theoretical air}} = \frac{\text{actual O}_2 - \text{theoretical O}_2}{\text{theoretical O}_2}$$

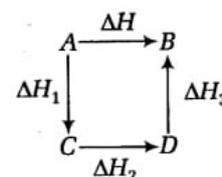
$$\text{Excess air factor} = \frac{\text{actual air used}}{\text{theoretical air}}; \text{ at 40\% excess air ;the value of excess air factor is 1.4}$$

Hess's law of constant heat summation:

Hess's law:

The law states that the change in enthalpy (heat) for a reaction is the same whether the reaction takes place in one or a series of steps.

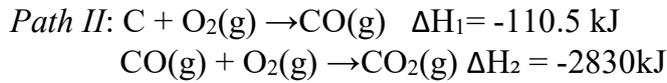
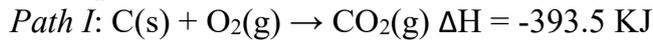
The Hess's law can also be stated as the enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs.



According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Example: Combustion of carbon dioxide can be done in two ways:



In both the cases, $\Delta H_1 + \Delta H_2 = 393.5 \text{ kJ}$

Kirchhoff's law: There are two laws.

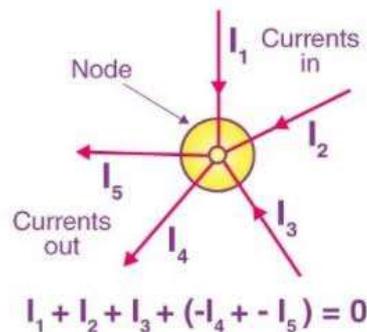
- a) 1st law (KCL)
- b) 2nd law (KVL)

a) Kirchhoff's current law (KCL):

Kirchhoff's current law states that total charge entering a Junction is equal total charge leaving it. Thus, it tells about the conservation of charge.

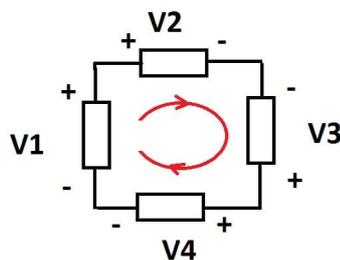
Incoming=Outgoing

$$I_1 + I_2 + I_3 = I_4 + I_5$$



At the node point, algebraic summation is zero.
 Kirchhoff's 1st law is related to conservation of current.

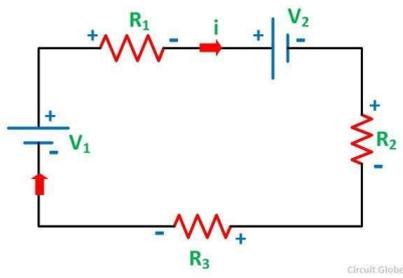
b) Kirchhoff's voltage law (KVL):



$$V_1 + V_2 + V_3 + V_4 = 0$$

$$\Sigma V = 0$$

2nd law (KVL) states that, in any closed path of an electric circuit the algebraic sum of all potential is zero.



$$V_1 + V_2 + (-IR_1) + (-IR_2) + (-IR_3) = 0$$

$$V_1 + V_2 = IR_1 + IR_2 + IR_3$$

(algebraic sum of voltage source = algebraic sum of voltage drop)

Kirchhoff's voltage law also states that the algebraic sum of voltage source is equal to the sum of voltage drop.

5.2. Combustion calculation:

Basic complete combustion reactions are: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$

C	+	O ₂	=	CO ₂
1 mole		1 mole		1 mole (molar or volume basis)
12 kg		32 kg		44 kg (mass basis)
H ₂	+	$\frac{1}{2}$ O ₂	=	H ₂ O
1 mole		$\frac{1}{2}$ mole		1 mole (molar or volume basis)
2 kg		16 kg		18 kg (mass basis)
S	+	O ₂	=	SO ₂
1 mole		1 mole	=	1 mole (molar or volume basis)
32 kg		32 kg		64 kg (mass basis)

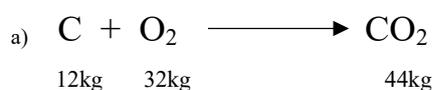
Important points to remember for combustion calculation:

Steps:

- 1) Write down combustion reactions for the elements present in the fuel.
- 2) Calculate the weight of oxygen required for combustion.
- 3) Subtract oxygens if already present in the fuel.
- 4) C, H₂, S, CO and hydrocarbons are the combustible substances present in fuel.
- 5) N₂, ash, CO₂ and water vapor are incombustible substances present in the fuel.
- 6) Calculate weight and volume of air.
- 7) In case of weight of air multiplication factor is 100/23 and in case of volume of air multiplication factor is 100/21.

Example 1. Calculate the weight and volume of air required for complete combustion of 1Kg. coal with following compositions, C = 85%, H = 10%, O = 5%.

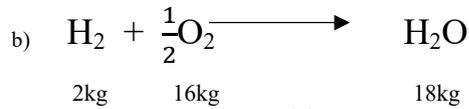
Solution: Combustion Reactions



For 1kg of C need $\frac{32}{12}$ kg O₂ for complete combustion.

In the fuel we have 85% C that is $\frac{85}{100} = 0.85$ kg of C

For 0.85Kg of C in coal, O₂ will be required = $0.85 \times \frac{32}{12} = 2.26$ kg



For 1kg of H₂ need $\frac{16}{2} = 8$ kg O₂ for complete combustion.

In the fuel we have 10% H₂ that is $\frac{10}{100} = 0.1$ kg of H₂

For 0.1Kg of H₂ in coal, O₂ will be required = $0.1 \times 8 = 0.8$ kg

Total amount of oxygen required = $2.26 \text{ kg} + 0.8 = 3.06$ kg

But, in fuel some O₂ is also present.

In the fuel we have 5% O₂ that is $\frac{5}{100} = 0.05$ kg of O₂

Final oxygen required is = $3.06 \text{ kg} - 0.05 = 3.01$ kg

Weight of air required for complete combustion is $3.01 \times \frac{100}{23} = 13.08$ kg (Ans)

Volume of air required for complete combustion:

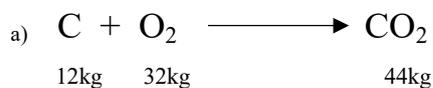
29 molecular weight of air have 22.4 lit volume in STP

So,

13.08 kg of air has volume of air = $13.08 \times \frac{22.4}{29} = 10.10$ lit (Ans)

Example 2. Calculate the amount of air required for theoretically complete combustion of 100kg of coal of the following composition, C = 82%, H₂ = 6%, O₂ = 4%, ash = 8%, S = 2%.

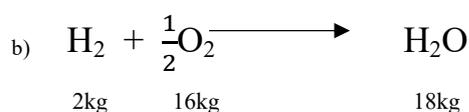
Solution: Combustion Reactions



For 1kg of C need $\frac{32}{12}$ kg O₂ for complete combustion.

In the fuel we have 82% C that is $\frac{82}{100} = 0.82$ kg of C

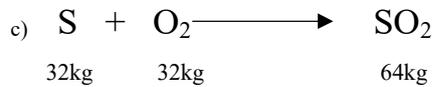
For 0.82Kg of C in coal, O₂ will be required = $0.82 \times \frac{32}{12} = 2.187$ kg



For 1kg of H₂ need $\frac{16}{2} = 8$ kg O₂ for complete combustion.

In the fuel we have 6% H₂ that is $\frac{6}{100} = 0.06$ kg of H₂

For 0.06kg of H₂ in coal, O₂ will be required = $0.06 \times 8 = 0.48$ kg



For 1kg of S need $\frac{32}{32} = 1$ kg O₂ for complete combustion.

In the fuel we have 2% S that is $\frac{2}{100} = 0.02$ kg of H₂

For 0.02kg of H₂ in coal, O₂ will be required = $0.02 \times 1 = 0.02$ kg

Total amount of oxygen required = $2.187\text{kg} + 0.48 + 0.02 = 2.669$ kg

But, in fuel some O₂ is also present.

In the fuel we have 4% O₂ that is $\frac{4}{100} = 0.04$ kg of O₂

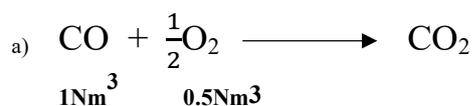
Final oxygen required is = 2.669 kg – 0.04 kg = **2.629 kg**

Weight of air required for complete combustion is $2.629 \times \frac{100}{23} = 11.43$ kg

For 100kg of coal air required = $11.43 \times 100 = 1143$ kg (Ans)

Example 3. Calculate the amount of air required for theoretically complete combustion of 100Nm^3 of blast furnace gas of the following composition (by volume), CO₂= 17%, CO=22.1%, H₂ = 4.9%, N₂= 55.8%, O₂ = 0.2%.

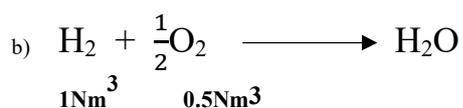
Solution: Combustion Reactions



For 1Nm^3 of CO need 0.5Nm^3 O₂ for complete combustion.

In the fuel we have 22.1% CO in 1Nm^3 of coal = 0.221Nm^3 of CO

For 0.221Nm^3 of CO in coal, O₂ will be required = $0.221 \times 0.5 = 0.1105$ Nm³



For 1Nm^3 of CO need 0.5Nm^3 O₂ for complete combustion.

In the fuel we have 4.9% H₂ in 1Nm^3 of coal = 0.049Nm^3 of H₂

For 0.049Nm^3 of H₂ in coal, O₂ will be required = $0.049 \times 0.5 = 0.0245$ Nm³

Total amount of oxygen required = $0.1105 \text{ Nm}^3 + 0.0245 \text{ Nm}^3 = 0.135 \text{ Nm}^3$

But, in fuel some O_2 is also present.

In the fuel we have 0.2% O_2 that is $\frac{0.2}{100} = 0.002 \text{ Nm}^3$ of O_2

Final oxygen required is = $0.135 \text{ Nm}^3 - 0.002 \text{ Nm}^3 = 0.133 \text{ Nm}^3$

Volume of air required for complete combustion is $0.133 \times \frac{100}{21} = 0.634 \text{ Nm}^3$

For 100 Nm^3 of coal air required = $0.634 \times 100 = 63.4 \text{ Nm}^3$ (Ans)

Assignment

1) A Sample has the following composition coal by weight $\text{C} = 78\%$, $\text{H}_2 = 6\%$, $\text{N}_2 = 2\%$, $\text{O}_2 = 9\%$, $\text{S} = 2\%$, ash = 3%. Find out the weight of air Required for complete combustion of 1kg of coal.

2) A coal has following composition by weight: $\text{C} = 80.3\%$, $\text{H}_2 = 5.7\%$, $\text{S} = 1\%$, $\text{N}_2 = 1\%$, ash = 12%. Calculate the amount of air required for complete combustion of 100 kg of coal.

3) A Sample has the following percentage composition coal by weight $\text{C} = 77.7\%$, $\text{H}_2 = 6.8\%$, $\text{N}_2 = 1.2\%$, $\text{O}_2 = 8.8\%$, $\text{S} = 2.2\%$, and incombustible = 3.3%. Determine the minimum quantity of air Required for complete combustion of 1kg of coal.

4) The percentage analysis by volume of a producer gas is $\text{H}_2 = 18.3\%$, $\text{CH}_4 = 3.4\%$, $\text{CO} = 25.4\%$, $\text{CO}_2 = 5\%$, $\text{N}_2 = 47.8\%$. Calculate the volume of air required per m^3 of the above producer gas for complete combustion.

6.Refractories

6. 1 Definition: Refractories are materials which withstand high temperature and do not fuse even at a very high temperature e.g. fire clay, silica, chromite, magnesite etc.

6.1 Classification. Three types of refractory materials exist depending upon their chemical nature as given below:

<i>Type of refractory material</i>	<i>Examples</i>	<i>Remarks</i>
Acidic refractory (silica is chief constituent) which readily combines with bases.	Fire clay, silica, Quartz, ganister sand, semi-silica, Alumino-silicate etc.	It should not be allowed to come in contact with basic products to avoid the reaction.
Basic refractory (consists of basic oxide without free silica)	Bauxite, magnesite dolomite, (lime is not used as refractory due to its dehydrating tendency), Alumina, Zirconia	Should not come in contact with acidic products.
Neutral refractory which does not combine with acids or bases.	Chromite, graphite carbon refractory, carbide, mullite, Kyanite, pure alumina	Can be used in conjunction with acidic or basic products.

Based on the method of manufacture, refractories are classified as:

- Dry pressed
- Fusion cast or electrocast
- Hand moulded
- Formed (Normal, fired/burned or chemically bonded)
- Unformed (Monolithics-plastics, Ramming mass, Gunning, Castable, Spraying)

ACID REFRACTORIES

Those refractories which are attacked by basic slags (.e. bases) are called acidic refractories and include:

- a) **Aluminium-silicate refractories** like fireclay bricks, high alumina bricks, kyanite, sillimanite, bauxite, diaspore, mulite, andalusite etc. These refractories vary widely in their physical, chemical and mineralogical characteristics depending on the nature and proportion of silica and alumina present in them. Free silica (SiO_2) should be as little as possible as it lowers the fusion point of these refractories. Addition of grog (ground pre-fired fireclay grains) improves the shrinkage properties of these refractories.
- b) **Silica refractories** consisting mainly of silica (and very low in alkalis and metallic oxide). Raw materials of various graded of silica refractories (containing silica upto 97%, alkalis $<0.3\%$ and alumina $< 10\%$) include natural rock, prepared mass quartz sand (ganister), quartzite, electrically fused quartz etc.

BASIC REFRACTORIES

Those refractories which are attacked by acid slags (acid) are called basic refractories and include:

- a) **Alumina (Al_2O_3)** refractories manufactured from burnt bauxite, electrocast bruxite or electro fused corundum.
- b) **Dolomite refractories** produced by calcining natural dolomite which is mainly a mixture of lime and magnesia.
- c) **Magnesite refractories** produced from dead burnt magnesite or magnesia (MgO). Chrome-magnesite and Magnesite-chrome refractories which are mixture of calcined magnesite and chromium oxide in various proportion necessary to develop required properties in them.

NEUTRAL REFRACTORIES

Those refractories which are not attacked either by basic slag/bases or acid slag/acids are called neutral refractories and include.

- a) chromite, carbon and graphite refractories
- b) artificially produced refractories like silicon carbide, zirconium carbide, titanium carbide etc.
- c) Metals used as refractory like thorium, tungsten, zirconium, platinum, nickel, iron, molybdenum, copper, vanadium, tantalum etc.

Alumino-silicate refractories are sometimes classified as neutral refractories but when exposed to basic slag, they exhibit acidic reaction.

INSULATING REFRACTORIES

A refractory suitable for minimising heat losses and thus achieving heat conservation in the furnaces is called insulating refractories. They have high porosity, low thermal conductivity and high thermal insulation properties and are produced from asbestos, fireclay, kieselguhr etc. At low temperature, slagwool, glasswool and vermiculite are also used as insulating materials. For high temperature thermal insulation applications foam ceramics and ceramic fibre and wool are used.

6.3 SPECIAL REFRACTORIES

These are very expensive refractory materials used for making crucibles and furnaces for special/experimental purposes where cost of refractory is no consideration. They are not very common due to their manufacturing limitation. Special refractories include pure oxides (e.g. magnesia, silica, alumina, beryllia, thoria etc), borides, nitrides, silicides, carbides etc. Other special refractories are Sialons, sircon, carborundum, alundum (a mixture of fused alumina and clay), sillimanite, electrocast blocks of mullite, magnesia and mixtures of chromite, bauxite and magnesia.

CERMET REFRACTORIES

This refractory is a combination of ceramic materials (e.g. oxide, nitride, carbide, borides etc.) and metallic/metallic alloys materials. It has the combination of good properties of both metallic and ceramic materials e.g. high strength and resistance to high temperature. Cermets are used in nuclear reactors, missiles and space crafts etc.

6.2 PROPERTIES OF REFRACTORIES

Important properties of refractories are resistance to high temperature, heavy load, fluxes, corrosive fluids like slag, thermal shocks due to rapid change in temperature (also called spalling resistance) etc.

Other properties are strength, specific gravity thermal and electrical conductivity etc.

Porosity and Slag Permeability. The higher the porosity of the refractory, the greater is the susceptibility of refractory to chemical attack of molten slags, gases etc. By decreasing the porosity, strength and thermal conductivity of the refractory is increased but spalling resistance (thermal shock resistance) is decreased the inner pore space for absorbing contraction and expansion is reduced.

Refractoriness or fusion point. It is the temperature at which the refractory fuses It should be much higher than the operating temperature of the refractory. Fusion point decreases when refractory is under load and this is called refractoriness under load (RUL).

Strength. It is the resistance of the refractory to compressive loads, tension and shear stresses. Refractoriness under load (RUL) is important as some refractories fail at a lower temperature when subjected to load. In taller furnaces, the refractory has to support a heavy load, hence strength under the combined effect of temperature and load is important.

Specific gravity. It should be low to produce more number of bricks per unit weight. Also lighter bricks in the lower part of a tall structure will not be subjected to a heavy load.

Cost of bricks of higher specific gravity is more than that of lower specific gravity (assuming the price of raw material being same per unit). Increase in bulk density of refractory increases its volume stability, heat capacity and resistance to slag penetration

Spalling. It is the fracture of refractory due to its uneven expansion on account of heat when they are subject to rapid heating and cooling. For reducing spalling, a refractory should be well fired and its porosity should be more.

Thermal Conductivity. Ordinary furnaces block should have low thermal conductivity but refractory used in coke oven, regenerators, muffle furnace should have high heat conductivity. Thermal conductivity is increased when the porosity of refractory bricks decreases i.e. when the air entrapped in refractory decreases. Insulating bricks (of low thermal conductivity) are maintained at high temperature and hence their life is short.

Electrical Conductivity. For electrical furnaces, the electrical conductivity of refractory material should be low. Except, graphite, all other refractories are had conductors of electricity. The electrical resistivity of the refractory drops rapidly with rise in temperature.

Chemical Composition. The chemical composition of the refractory should be such that the surroundings do not chemically attack the refractory and corrode it. Acidic refractory should not be used in a furnace heating a basic material, otherwise the brick will react with the furnace stock and get eroded and hence its life will be reduced.

Slag Resistance. Slag attacks the refractory particularly at high temperature by forming mixture or new compounds with the refractory substance in contact with. Slag dissolves some of the refractory material and forms a viscous slag film whose melting temperature may be higher or lower. Resistance of refractory to slag action depends on the nature of slag and the refractory. Relative resistance of various refractories depend upon temperature, change in slag composition (on combining with refractories) and the nature of contact with the slag i.e. whether the slag is moving, stationary or is carried as fine particles by the gases/flame.

A basic slag attacks an acidic refractory while an acid slag attacks a basic refractory very rapidly. Rate of slag attack is accelerated by the following factors

- i. defective joints and cracks in the refractory structures.
- ii. presence of fusible glass of refractories
- iii. rough and porous surfaces of refractories
- iv. moving slag as compared to stationary slag.

Rate of slag attack is reduced, if the refractory is dense and well vitrified (c.a. offering smoother surface) and the slag is stationary.

Abrasion Resistance. A refractory is subjected to wear, when it comes in contact with a moving charge and in case of blast furnace, descending charge materials result in abrasion wearing away of the refractory lining material. Abrasion resistance of refractory is increased by using a dense (low porosity), fine grained and wear resistant refractory lining.

Erosion Resistance. Erosion (damage due to mechanical action) occurs when metal or gas carrying dust and slag particles hit against the refractory lining resulting in 'chipping off' of particles from the refractory. Splashing of slag erodes the refractory lining whereas slag particles entrained by flame/gases erode particularly the arches and bends of the structure.

Size and Shape. It is a part of the design of furnace, since it affects the stability of the furnace structure. Accurate refractory size is important to properly fit the refractory shape inside the furnace and to minimise space between construction joints.

6.3 SELECTION OF REFRACTORIES

The selection of refractories for any particular application is made with a view to achieving the best performance of the equipment, furnace, kiln or boiler and depends on certain

properties of the refractories.

Further, the choice of a refractory material for a given application will be determined by the type of furnace or heating unit and the prevailing conditions e.g. the gaseous atmosphere, the presence of slags, the type of metal charge etc. Therefore, temperature is not the only criterion for selection of refractories.

Any furnace designer or industry should have a clear idea about the service conditions which the refractory is required to face. The furnace manufacturers or users have the following points, before selecting a refractory to consider

- Area of application.
- Extent of abrasion and impact.
- Stress due to temperature gradient in the structures and temperatures fluctuations
- Working temperatures:
- Structural load of the furnace.
- Chemical compatibility to the furnace environment.
- Heat transfer and fuel conservation.
- Cost considerations
