Fuel and Energy Technology

(PECH 5301)

(B.Tech, 5th Semester)

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PECH 5301	**FUEL AND ENERGY TECHNOLOGY**	**3L-0T-0P**	**3 Credit**

Course Objectives:

- To provide comprehensive knowledge of solid, liquid and gaseous Fuel.
- To study synthetic fuel and nuclear fuel.

Module 1 (4Weeks/12 Hours)

Unit I: Fuels: Solid Fuels: Coal - Origin, chemical composition, calorific value, classifications, Characteristics& distribution of Indian coals, storage and spontaneous combustion of coal.

Unit II: Coal washing and blending, petrographic constituents of coal, carbonization of coal, manufacture and properties of metallurgical coke, recovery of by-products.

Module-2 (4Weeks/12 Hours)

Unit III: Liquid Fuels: Origin and composition of crude oil, crude oil distillation and its products with special reference to gasoline, kerosene and diesel oil, cracking and reforming, coal tar distillation products, Shale oil.

Unit IV: Gaseous Fuels: Natural gas, coal gas, coke oven and blast furnace gas, manufacture of water gas and producer gas, carbureted water gas.

Module -3 (4Weeks/12 Hours)

Unit V: Synthetic Fuels: Hydrogenation of coal, Fischer–Tropsch synthesis.

Unit VI: Nuclear Fuels: Introduction, nuclear fuels and nuclear reactors, moderators and structural materials. Introduction to renewable energy sources.

Module IV: (2Weeks/6 Hours)

Unit VII: Combustion: Combustion of solids fuels, calculation of volumes and weights of air necessary for combustion of fuels, gas analysis

Text Books:

1. Fuels and Combustion, 3rd ed. by S Sarkar, Universities Press.
2.Elements of Fuels, Furnaces & Refractories by O P Gupta, Khanna

3.The Elements of Fuel Technology, 2nd ed. by G W Himus, L Hill.

4. Fuel Solid, Liquid and Gaseous, 4th ed. by J S SBrame and J G King, Edward Arnold.

Course Outcome:

On successful completion of the course, the student will be able to

- Understand the different types of fuel.
- Analyze problems involving calculation of volumes and weight of air necessary for combustion of fuels.

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Dr. Sudip Banerjee

Solid fuels (Module-1)

❖ Introduction

Any naturally occurring carbon-containing material, when burned with air (or oxygen) produces heat or energy (directly or indirectly). Fossil fuels can be classified according to their respective forms at ambient conditions. Thus, there are solid fuels (coals), liquid fuels (petroleum) and gaseous fuels (natural gas, LPG etc.).

❖ History of solid fuels

Coal is a brown to black naturally occurring combustible organic rock that originated by accumulation and subsequent physical and chemical alteration of plant material over long period of time. The plant debris accumulated in various wet environments, commonly called peat swamps, in which trees, ferns and the like are deposited, and buried by sand, silt and mud. As a result of temperature and pressure effects, metamorphosis of the woody material occurs to produce the various types of coal. The initial transformation of vegetable materials probably includes various types of degradation and decay due to some fungal and bacterial action. Slow atmospheric oxidation may also take place. The course and rapidity of the vegetal decay are the function of local conditions, either dry or wet. The accumulating spongy, water-saturated, plant-derived organic material, known as peat, is called the precursor of coal. This is primary transformation. The secondary transformation which is rather a slower process of aging under substantially anaerobic condition, higher pressures and elevated temperature. This progressive transformation of peat to higher coals is called coalification process. Increasingly deeper burial under hundreds to thousands of feet of younger sediment is required to advance coalification to the bituminous and anthracite stages. The pressure exerted by the weight of the overlying sediments and the heat that increases with depth, as well as the length of exposure to them, determines the degree of coalification, as well as the rank of coal.

There are two theories proposed for the mode of accumulation of the plant materials to transform into coal.

- ***In-situ theory***-According to this theory, the coal seams are observed where once forest grew. As the land was sinking slowly, the accumulated vegetation matters went under water slowly and did not decompose and destroyed. In the course of time, the rate of sinking of land was increased and coal forest was submerged under water. Again, land along with the coal forest emerged out of water after sufficient time and this cycle went on again and again, which is responsible of formation of coal strata and seams. The evidence of this phenomenon is observed in the coal seam that the stem of fossil trees is found standing erect with their roots protruding into the under-clays. The uniformity in thickness and composition of coal seams over wide areas suggests that the deposition of plant material took place in still water.
- ***Drift theory-*** This theory tells that, the plant material was transported with the stream of water from one place to another, and finally get deposited in a place of swamp having suitable condition like sediments. The coal seams of India are of drift origin. The evidence of drift theory that the rocks associated with the coal seams are of distinctly sedimentary. The coal seam itself behaves like a sedimentary bed and they are observed to branch out. Peat transforms into coal by the sequence, as shown in **Fig. 1**,

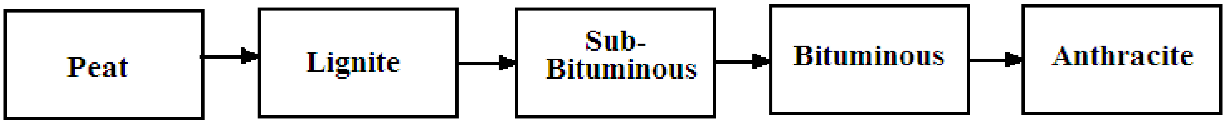


Fig. 1. Rank of coal

It is assumed that, at least some of the natural graphites are produced from anthracite by the effect of very high temperature (not shown in figure). Although samples of each rank of coal have distinct physical and chemical characteristics, the border line between two consecutive ranks of coal is difficult to determine. The first four samples in the series have a nearly continuous gradation of a given physical and chemical properties, such as moisture content, carbon content, heat content etc.

Peat is the result of insufficient transformation. The composition and properties of peat vary greatly from one place to another, depending on the nature and type of the original plant material and the extent of decay. It contains very large amount of water. Peat is not regarded as coal, but it is an important fuel in those countries which have large deposits of peat. It is mainly used as a domestic fuel. Moreover peat briquettes are largely used in steam boilers, power stations and gas producers. It ignites easily with a long flame. Lignite, may be termed as Brown coal, is lowest in rank and readily identified by its colour and texture. It is soft, has a woody structure and disintegrates on drying. Dark brown or black colour is observed in lignite, having woody and amorphous nature. Lignite breaks in slabs after long time exposure to weather. It is characterized by a high percentage of moisture, ranging from 30-50% with high oxygen content. Black lignite grades are the preliminary stage of sub-bituminous coal, having of lower oxygen content and higher heating value than lignite. Sub-bituminous coals are not distinguishable as a class by appearance or physical properties. They are intermediate between black lignite and bituminous products. Sub-bituminous coals slowly disintegrate on exposure to atmosphere. Different bituminous coals vary in their appearance and properties. In general, they are harder than sub-bituminous samples and exhibit cubical fracture in most of the time.

Next rank is anthracite coal which is again harder than bituminous and having an amorphous texture. Anthracite is relatively dustless solid coal and burns with a smokeless flame. High carbon content and low volatile matter and oxygen are the characteristics of anthracite coal. As the rank of coal increases from peat to anthracite, the carbon content increases but, moisture, volatile matter and oxygen contents decrease. The carbon content increases from 70% to 95% from lignite to anthracite coal. The chemical composition of coal is not very clearly known. It is generally said that, coal components are macromolecular with complex structures. The reason for appearance of different components in different rank of coal is the variation of the structures of these macromolecules. Waxes, resins, pectin, hemicelluloses, lignite etc. are found in low rank coal as peat and lignite. The major coal fields in India are Gondwana coal field and Tertiary coal field. Gondwana coal field covers the areas of West Bengal, Bihar, Orissa, Madhya Pradesh, Maharastra, Andra Pradesh etc. Tertiary coal field covers North East India, Tamilnadu, Rajasthan, J&K, Gujarat etc. More than 98% coal is obtained from Gondwana coal field. Vast reserves of bituminous coal are found in Raniganj and Bokaro-Ramgarh-Karanpura deposits in Gondwana coal field. Raniganj coal measures are high in moisture (3-10%) and high in volatile matter (30-36%). The coals of Gondwana basins are mainly of sub-bituminous type. Coalfields of the Damodar valley of Jharkhand and Bihar are the chief source of metallurgical coal in the country and most of the iron and steel plants get coking coal from these fields.

❖ Definitions and properties of solid fuels

Coal varies widely in composition and properties and they are used in different conditions. Coal characteristics are determined by various kinds of analytical and testing data, which are of scientific, technical and commercial interest. Following are the definitions of some coal characterization and analysis.

- **Ultimate and Proximate analysis of coal**

Ultimate analysis is the elemental analysis which determines the percentage composition of carbon, hydrogen, oxygen, nitrogen and sulfur by weight. These elemental compositions are of pure fuel only, which is free of moisture and inorganic compounds. Proximate analysis reports moisture, volatile matter, ash and fixed carbon content of a fuel by percentage weight, as defined by ASTM D 121. Moisture is the amount of water obtained from the fuel by heating at a specific condition according to the standard method, without making any chemical change to the fuel. Volatile matter consists of gases and vapors driven off during pyrolysis under specified condition minus moisture, fixed carbon is the nonvolatile fraction of coal, and ash is the inorganic residue remaining after combustion. Proximate analysis is the most often used analysis for characterization of coals.

- **Gross and Net calorific value**

When coal is heated at high temperature in presence of air, heat liberated per unit weight of fuel is called heating value or calorific value of that fuel. Calorific value can be determined either at constant volume or constant pressure. Gross calorific value at constant volume is the amount of heat liberated by combusting unit weight of coal at constant volume in an atmosphere of water vapour saturated oxygen, the original fuel and final products of combustion should be at 25^0C and the water obtained by this process should be in liquid state. Gross calorific value at constant pressure is similar to that of constant volume, only difference is that, the combustion occurs at constant pressure. Net calorific value at constant volume is the amount of heat liberated by combusting unit weight of coal at constant volume in an atmosphere of water vapour saturated oxygen, the original fuel and final products of combustion should be at 25^0C and the water obtained by this process should be in vapour state. Net calorific value at constant pressure is that, the combustion occurs at constant pressure, not constant volume. Gross calorific value is also called higher heating value as it is higher than net calorific value. The reason for this is, while determining net calorific value, the water remains in vapour state, hence the heat of condensation is not taken in consideration, which is rather a part of gross calorific value where water obtained is in liquid phase.

- **Ash content**

Ash in coal, which is the remains when coal is burnt, is one of the materials of interest. Ash is derived from the mineral matter content of coal. The inorganic materials which were actually the part of the plant structures, constitute the ‘inherent’ mineral matter of coal, whereas, the ‘extraneous’ mineral matter is that which was introduced probably as air-borne dusts or waterborne silts at the later stage of coalification. Mineral matter of coal predominantly consists of kaolinite, pyrite and calcite and upon combustion; results in the oxides of silicons and metals, such as, aluminium, iron and calcium. These oxides are the essential part of ash. When coal burns, shales and other hydrated materials, which are also the constituents of mineral matter of coal, decompose and lose their water of hydration and also emit carbon dioxide, sulfur dioxide gases. As there is a loss in weight, so, amount of ash of coal is always less than its mineral matter content.

- **Moisture content**

Moisture of coal may also become inherent or extraneous. Inherent moisture is the moisture associated with coal inherently, which cannot be removed by only air drying, it can be removed when coal is heated above 100^0C. Extraneous moisture can be removed by air drying of coal.

- **Volatile matter**

Volatile matter is the volatile part of coal when coal undergoes thermal decomposition. The volatile part of organic mass of coal is the main constituent of it. The moisture content of coal is not included in it. But volatile matter of may contain water, when hydrogen and oxygen of coal produce water at high temperature of decomposition. The water of hydration, which is liberated during decomposition, is also a part of volatile matter. It is observed that, as the maturity of coal increases, volatile matter decreases. Fixed carbon is the non-volatile part of organic mass after decomposition. Ash is not included in it. Fixed carbon should not be confused with the total carbon of coal. In anthracite, the values of fixed carbon and total carbon are almost equal, whereas, for other coals, fixed carbon is less than total carbon. The major elements present in coal are carbon, hydrogen, oxygen, sulfur and phosphorous. There are different methods to determine their content.

❖ Coal carbonization, caking index and swelling index

Coal carbonization is the process where coal is heated at high temperature without contact of air. The decomposition product is of higher carbon content than the original coal. When coal is converted to gaseous fuel by heating at sufficiently high temperature, the process is called gasification of coal. During carbonization, some gaseous products are also produced. During carbonization, some types of coal can produce lumps from its pulverized form. These lumps are called cake and the process of cake formation is called **caking**. When these lumps can meet the specification of some standard tests in terms of its hardness, brittleness etc. and also its suitability to use in steel industry as a source of heat as well as a reducing agent, then they are called **coke**. **Coke is prepared in commercial coke oven by the process of carbonization at more than 1000^{0}C.** This carbonization process is called coking. All types of coal do not show caking property. Some types of bituminous coals are caking in nature. Other coals are non-caking. Hence, caking property of a coal is important for selection of a particular type of coal in industrial purpose. Caking index is determined for coal to obtain its binding or agglutinating property. This is defined as the maximum whole number ratio of sand to coal in a 25 g mixture of those two, lumps produced by heating that mixture at a specified condition which can withstand a 500 g weight, and the loose particles obtained by this process should not exceed 5%. Swelling index is another important property of coal, where it is heated under specified condition. The residue obtained is a swollen mass due to volatiles in coal are driven off. This mass is compared with a standard chart where pictures of different swollen mass are given with a definite number or unit, starting from 0 to 9, with an increment of ½. The number of the picture with which the swollen mass matches is its swelling index.

❖ Fundamental definitions, properties and various measurements

- **Various measurement techniques**

Characterization of coal and petroleum fractions, as well as gaseous fuels is done by some specific test methods and apparatus. Some major characterization techniques are mentioned in this section. Some standards, such as ASTM (American Society for Testing and Materials), BS (British Standard), IS (Indian standard) etc. are followed to determine the properties.

- **Measurement techniques for coal and coke**

Proximate analysis of coal is an important analytical technique to determine moisture, volatile matter, ash and fixed carbon content in terms of weight percentage. In this method, a specific amount of finely powdered coal (1 or 2 g) is heated in a petri-dish for one hour at 105 to 110^{0}C, sample is cooled and weighed. The weight loss is the external moisture content. The coal sample is then taken in a silica crucible and heated at 925^{0}C for 7 min, the sample is quickly cooled to avoid the oxidation and then weighed. The weight loss is expressed as volatile matter content. About 1 g of powdered coal is taken in a silica dish and heated in a muffle furnace at 400 to 450^{0}C for 30 mins, and then one hr at 725±25^{0}C. The weight of the incinerated residue is the ash content. The fixed carbon is obtained by subtracting the weights of moisture, volatile matter and ash content from 100.

Caking index for coal is determined by taking sample of the uniform mixtures of sand and coal of total 25 g in different weight ratios. The samples taken in crucibles are kept inside a muffle furnace at approximately 925^{0}C for 7 min. Then the crucibles are removed and allowed to cool. The lump or cake is observed to form from the mixtures. The cakes are taken out carefully and 500 g weight is placed on the cakes. The percentage of loose particles comes out from the cakes are determined separately for each cake which gives a measure of the binding property of the coal sample. The maximum whole number ratio of sand to coal in the 25 g mixture which produces a cake after heating that can withstand a weight of 500 g without producing 5% loose grain is the caking index.

Swelling index is one of the important properties of coal. Coal is heated under specified condition on flame in a crucible. The swollen mass is cooled and compared with a standard chart where profiles with numbers (which indicates swelling index) are given. The numbers are in increasing order from 0 to 9 with a 0.5 increment. The higher the number better is the caking and swelling characteristics.

Calorific value of coal is determined by Bomb calorimeter. It is a thick walled steel cylindrical vessel with lid which is called Bomb. Two electrodes are inserted through the lid which are in contact with fuse and fuel sample of known weight. An oxygen inlet valve is provided with the lid through which high pressure oxygen gas (at about 25 to 30 atm) is supplied. Entire arrangement is held in a calorimeter containing known weight of water and a mechanical stirrer is provided to stir the water for uniform heating. A Beckmann thermometer is also provided to measure the change in temperature of water due to combustion of fuel. Fig 2. shows the schematic of the apparatus. The gross calorific value is calculated by the following formula

$$C.V = (m_1 + m_2)(T_C + T_1 - T_2)C_w / m_f$$

Where, m_1 and m_2 are mass of water in calorimeter and water equivalent of bomb calorimeter respectively. m_f is mass of fuel sample whose calorific value is to be determined. T_1 and T_2 are final and initial temperature of water sample. T_c is temperature correction for radiation losses. C_w is specific heat of water.

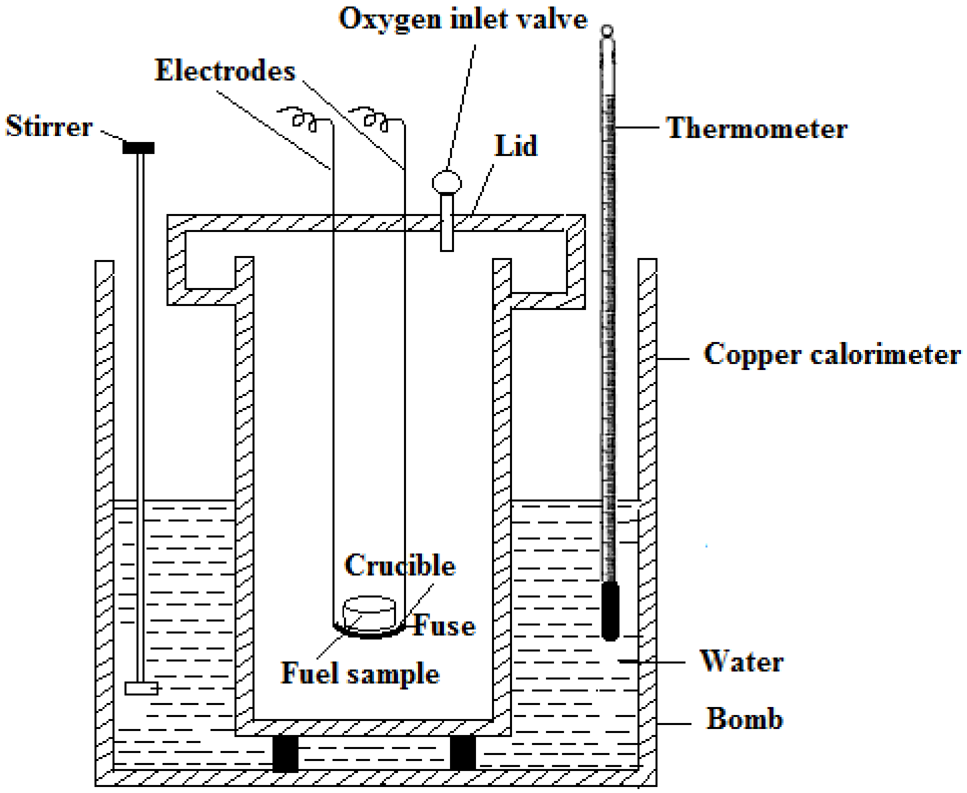
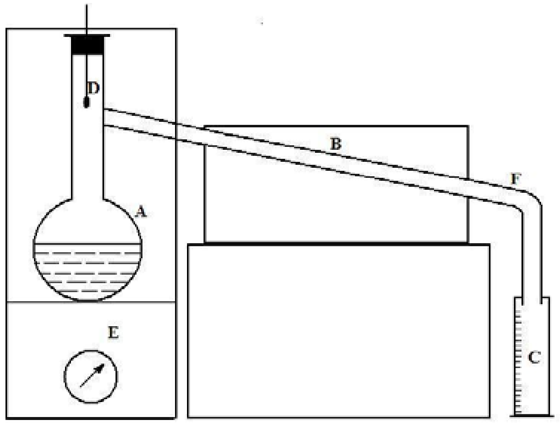


Fig. 2. Bomb calorimeter

The major property of coke is its strength and hardness. Among many tests to determine strength and hardness of coke, Micum test is important. In mecum test, 50 kg of coke samples are taken in a metallic cylindrical drum (Micum trommel) of 1 m length and 1 m diameter, and the drum is rotated about its horizontal axis at 25 rpm speed for 4 min. Iron angles are provided inside the drum wall. This rotation gives a combined effect of abrasion and shatter to coke samples. The particle size distribution after the test is determined by sieve analysis and this gives the account of brittleness of coke during its handling and use. Micum index or M80 denotes the percentage weight of coke lumps greater in size of 80 mm.

- **Measurement techniques for petroleum fractions**

Distillation or vaporisation characteristics of a petroleum cut is determined by following ASTM method (ASTM D-86). This is the method of non-fractionating atmospheric distillation of light cuts such as, gasoline, kerosene etc. A specific amount of liquid fuel is taken in a standard round bottom flask with the arrangement of condenser and thermometer device. **Fig**. 3. shows the standard set-up , consisting of a flask, condenser, collector and thermometer. The fuel is heated by an electric heater at a specified rate and some part of vapour flows to the condenser through the side limb of the flask. Other part of the vapour gets condensed and flows down as liquid to the flask which acts as reflux. The condensed vapour from condenser is collected in the collector. The volume percent distilled is plotted against corresponding temperature which provides the vaporization characteristics of the particular fuel.



A= Flask, B= Condenser, C= Collector, D= Thermometer, E= Controller switch
Fig 3. ASTM distillation apparatus

Flash point and fire point of a definite petroleum cut are measured in a standard apparatus. Different fractions may be classified based on their flash point, such as, fractions below 23^0C flash point are highly inflammable, dangerous, between 23 to 66^0C are moderately inflammable and above 66^0C are termed as safe. Gasoline lies in the first category, kerosene in the second and higher oils, such as fuel oil and gas oils fall in the third. Abel apparatus is used for the oils having flash point below 50^0C and Pensky-Martens apparatus is used for the oils having flash point above that temperature. Both these apparatus are of closed cup type. A specified amount of oil is heated in a definite rate in a closed cup. A provision is made to remove a shutter to escape the fuel vapor and air mixture and an external flame is introduced to test the flash. The temperature of the oil is determined by a thermometer at the time of flash. That is the flash point of the oil. Flash point of heavy oils such as lubricating oil, crude oil or residue can be obtained by Pensky-Marten open cup or Cleveland open cup apparatus.

Pour point and cloud point of oil is determined by putting the oil in a specified test tube, where thermometer is inserted. The oil is cooled at specified rate and at short interval of time the oil is tested by tilting the test tube to see whether the oil is totally freezed. The maximum temperature where oil does not show any flow, that temperature is recorded and the reporting of pour point is done by adding 2.8^0C or 50F to that. Before that freezing temperature comes, haziness on the top of the surface of the oil appears and that temperature is the cloud point of the oil.

Smoke point of kerosene is determined in a standard apparatus (**Fig.** 4) where kerosene is poured in a specified holder (B) with wick on its top. The wick is lit and the height of its flame is so adjusted that it gives a flame with round top, without any shoot tail. The maximum flame height is measured by a mirror scale (C) at the back of the flame in the instrument. An exhaust (D) is provided at the top of the apparatus. A lid with glass cover (A) is used to cover the flame from wind.

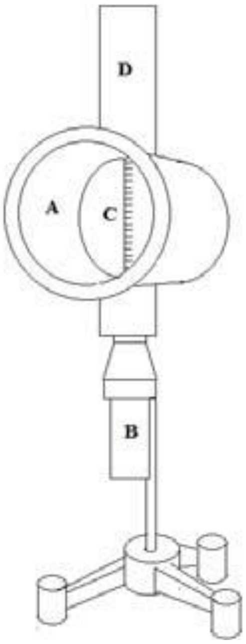


Fig.4 Smoke point apparatus

Burning quality of kerosene is determined by its char value. A standard lamp with glass chimney is used. Definite amount of kerosene is poured in the lamp and wick is lit. The lamp is allowed to keep lit for continuously 24 hours. The flame heights, initially and finally, are measured by the graduation on the chimney. The char deposit on the wick is scraped and weighed. The mg of char per kilogram of kerosene burned is expressed as char value of that kerosene. The decrease inflame height is also a measure of the quality of kerosene.

Measurement techniques for gaseous fuel

Compositional analysis of a gas mixture is done by Orsat apparatus as shown in **Fig. 5**. It is a standard apparatus in which normally carbon dioxide, carbon monoxide, oxygen and nitrogen gas composition in volume percentages are reported. Sometimes, hydrogen, methane and unsaturated hydrocarbons can also be quantified in this apparatus. The apparatus consists of a graduated burette upto 100 divisions from bottom to top, an aspirator bottle, a series of pipettes having necessary fittings and a three way stop-cock connecting the top of the burette to the gas stream. Each pipette contains an adsorbent for removing one gas. The adsorbents used are caustic potash solution, freshly prepared alkaline pyrogallol solution and cuprous chloride in ammonia solution for removal of CO_2, O_2 and CO respectively. Unsaturated hydrocarbons can be removed by using bromine solution. The measured gas sample is passed to the pipettes one by one, by opening the stopcock and raising and lowering the aspirator bottle several times for ensure proper adsorption of gases in the respective adsorbents. The decrease in volume from the initial volume after passage through every pipette gives the account of volume percent of the respective gas. Fig.4 shows the typical figure of Orsat apparatus, where A is the graduated glass tube and E, D, C and B are the pipettes containing KOH, alkaline pyrogallol, bromine solution and ammoniacal cuprous chloride solutions respectively, F is the stopcock, G is aspirator bottle, H is rubber tube.

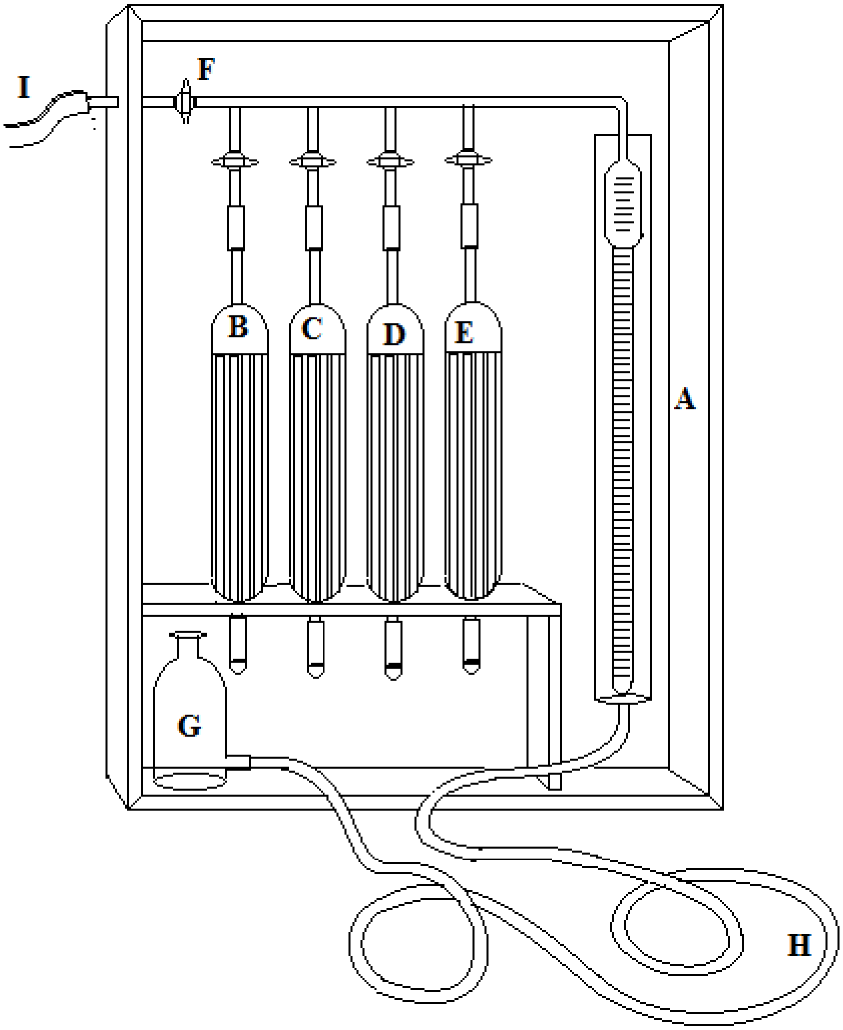


Fig. 5. Orsat Apparatus

The gross calorific value at constant pressure of a gaseous fuel is determined by Junkers calorimeter. The method is based on heating a particular amount of water by the heat evolved by burning of the gaseous fuel. The calorific value is calculated by the following formula

$$C.V = \frac{w * T * C_{P,water}}{V * K}$$

Where, w= weight of hot water collected in kg, V= observed gas volume in m^3, T= temperature rise of water in ^{0}C, $C_{p,\ water}$ = Specific heat of water in kCal/kg.K, and $K=[(P_a+P_g-P_w)$ in mm Hg/760 mm Hg]×273/(273+t), where, P_a and P_g are the atmospheric and gauge pressure of gas, P_w is saturated vapour pressure of water at the temperature of the system, t (^{0}C).

- **Definitions and properties of liquid and gaseous fuels**

The composition of petroleum varies with the location, age and also individual well. The high proportion of carbon and hydrogen indicate that hydrocarbons are the major constituents of petroleum. The principal types of hydrocarbon present in crude oil are normal, branched or cyclic saturated hydrocarbons, aromatic hydrocarbons or compounds with molecular structure associating both these basic types. The properties of crude petroleum and its fractions can be determined by various ways. Crude oils are roughly classified into different bases according to the nature of principal type of hydrocarbons present in it. The bases are paraffin base, naphthene based, mixed base or intermediate base and aromatic base. Paraffin based crude oils composed of mainly paraffins. Mixed base or intermediate base crudes are lower in n-paraffins and higher in naphthenes compared to that of the paraffin base oils. Naphthene base crudes are characterized by a high percentage of naphthenes and almost no presence of any wax. Aromatic base crudes contain a relatively high percentage of the lower aromatic hydrocarbons. This classification is arbitrary, but long use of this concept makes this classification valuable to the technical persons. **^{0}API or API gravity** is an empirical correlation which is actually a representation of specific gravity of petroleum crude or cuts (fractions). It is defined by **American Petroleum Institute (API)**, as

$$API\ \ Gravity = \frac{141.5}{sp.gr.\left(\frac{15.5^{\circ}C}{15.5^{\circ}C}\right)} - 131.5$$

API gravity is used in petroleum chemistry instead of specific gravity. This is because; the petroleum cuts are having specific gravities which are very near to each other. But use of API gravity makes the difference of gravity wider between the two consecutive cuts, as specific gravity is in the denominator in the expression of API gravity.

Vaporisation characteristics of petroleum cuts are obtained by distilling a definite volume of the fraction in a specified apparatus. As petroleum cuts are the mixture of different hydrocarbons, they do not have a definite boiling point, but have a boiling range. Initial boiling point (IBP) of a petroleum cut is the temperature when first drop of distillate comes out of the condenser of the distillation apparatus. Final boiling point (FBP) is the maximum temperature recorded at the end of the distillation. Distillation cannot be carried on beyond 350^0C temperature at atmospheric pressure, because at this temperature, cracking of the hydrocarbons starts. Boiling range of a petroleum cut is important in evaluating it.

Viscosity index is a property of petroleum fractions, which is defined as the rate of change of viscosity with temperature. This is indicated by a number in an arbitrary scale ranging from 0 to 100, higher the number more is the viscosity index. A viscosity index of 100 means, oil which ideally does not become thin at elevated temperatures or become viscous at lower temperature. Mainly paraffinic base lubricating oils exhibit a viscosity index near 100.

Flash point and fire point are the two important properties of petroleum fractions. Flash point is defined as the minimum temperature at which the fuel upon heating evolves vapour which after mixing with the air give a sudden flash when a source of fire is brought in contact with it. Fire point is the minimum temperature at which the fuel vapour in admixture with air will produce a continuous fire when a fire source is brought in contact with the vapour. So, the fire point is more than the flash point for a particular petroleum fraction. Hence, flash point is more important than fire point in view of any fire hazard.

During the transportation of heavy oil fractions in pipelines, there is a possibility of freezing the oil within the pipe when it is transported at cold climate. Here **pour point and cloud point** are the two properties of these oils which play important role. Pour point is the maximum temperature, at which oil ceases to flow when it is cooled at specified condition. Pour point is reported by adding 2.8^0C or 5^0F to this temperature, which is a caution to technical people.

Cloud point is the temperature at which oil becomes cloudy, when it is cooled at a specified condition.

Burning quality of kerosene can be determined by its illuminating capacity and it is expressed by two properties, smoke point and char value. Smoke point is defined as the maximum flame height in millimeters when kerosene burns in a standard apparatus without producing any smoke or shoot. Char value is the amount of char produced in milligrams on the wick of a standard apparatus per kilogram of kerosene burned.

Carbon residue is the important characteristic of the oils which are used in engines, burners and furnaces. The carbonaceous residue obtained after heating the oil at a specified rate due to cracking and decomposition is called carbon residue. Two different types, **Conradson** and **Ramsbottom** carbon residue were determined, depending on the methods followed.

Octane number determines the quality of gasoline or petrol. When gasoline is burned in a spark ignition engine (petrol engine), it produces power. A good quality gasoline burns smoothly without making any noise in the engine. Whereas, burning of a bad quality gasoline is not smooth and produces a sudden high pressure by burning all fuel at a time, which forms pressure wave or detonation or knock to the engine. The octane number of a gasoline is a measure of knocking tendency. Octane number is determined by comparing the performance of a model fuel and the gasoline under test in a standard engine in laboratory. The model fuel is prepared by mixing iso-octane (2,2,4 trimethyl pentane) whose octane number is assumed to be 100 and nheptane, whose octane number is assumed to be zero. So, octane number of a gasoline sample is defined as the percent by volume of iso-octane in a model fuel (mixture of iso-octane and nheptane) whose knocking performance matches with the test gasoline. Hence, a gasoline with octane number 90 means, its knocking tendency matches with a model fuel having 90 vol% isooctane.

The descending order of octane number of the hydrocarbons is: **aromatics> isoparaffins> naphthene> olefins> n-paraffins**. There are many octane number improvers. **Tetraethyl lead (TEL)** is the most common improver. Now-a-days, octane number is improved by adding alkylates to gasoline.

Ignition quality of diesel is expressed by **cetane number**. Diesel is injected in the hot compressed air in the cylinder of a diesel engine, which then burns to produce power. If there is a large time gap between the injection and ignition, there is an unwanted accumulation of fuel in the cylinder, which suddenly burns at a time with a pressure wave, producing diesel knock. Like octane number, here also a model fuel is prepared by mixing n-hexadecane or cetane (whose cetane number is assigned to 100) and ∞-methyl naphthalene (whose cetane number is assumed to be zero), at different volume proportions. The performance of the diesel under test is compared with the model fuel. The percent by volume of n-hexadecane in a model fuel is the cetane number of the test diesel whose diesel knocking performance matches with the model fuel when tested in a specified engine. Hence, if the performance of test diesel matches with the performance of the model fuel having 45/55 blend of cetane and ∞-methyl naphthalene, then the diesel is assigned to cetane number of 45. The descending order of cetane number of hydrocarbons is just reverse to that of octane number.

Aniline point is also a property mainly of diesel. This is defined as the temperature at which the oil under test is completely miscible with equal volume of aniline, when tested in a standard apparatus. Aromatics dissolve aromatics easily. Hence, if the oil contains more aromatics, its aniline point will be low. But if the oil contains more paraffin, its aniline point will be more.

Diesel index is an empirical index which is defined as

$$Diesel\ index = \frac{Aniline\ point,\ ^{\circ}F \times\ Degree\ API}{100}$$

Usually, it is observed that diesel index is three units higher than the cetane number, although it is not exactly the same for all the cases. Petroleum cuts contain ash but to a very negligible amount. Moisture content is also very less which can be determined by standard test. Sulfur in petroleum oils remain in the form of sulfides, disulfides, marcaptans, thiophenes and higher thiophenes. Heavier the cut more is the sulfur content.

Calorific value of both petroleum oil and gaseous fuel are determined by bomb calorimeter and Junker's calorimeter. The gross calorific value of petroleum cuts vary from 10000 to11500 kcal/kg, the lower boiling cut, such as gasoline shows higher value and heavier oils show lower value. Among gaseous fuels, natural gas and LPG has highest calorific value, which is in the range of 43000 to 46000 kJ/m^3. Other gaseous fuels are of moderate or low calorific value, such as the calorific value of producer gas, carbureted water gas and coal gas are 5000, 19000 and 20,000 kJ/m^3 respectively.

❖ Coal classification, composition and basis

Coal is called a fossil fuel because it was formed from the remains of vegetation that grew as long as 400 million years ago. Most of our coal was formed about 300 million years ago, when much of the earth was covered by steamy swamps. As plants and trees died, their remains sank to the bottom of the swampy areas, accumulating layer upon layer and eventually forming a soggy, dense material called peat. Over long periods of time, the earth's surface changed, and seas and great rivers caused deposits of sand, clay and other mineral matter to accumulate, burying the peat. Sandstone and other sedimentary rocks were formed above peat layer, and the pressure caused by their weight squeezed out the water from the peat. Increasingly deeper burial and the heat associated with it gradually changed the material to coal. Scientists estimate that 3 to 7 feet of compacted plant matter was required to form 1 foot of bituminous coal. There are many compositional differences between the coals mined from the different coal deposits worldwide. Coal formation is a continuing process and some of our newest coal is a mere 1 million years old. Today, in areas such as the Great Dismal Swamp of North Carolina and Virginia, the Okefenokee Swamp of Georgia, and the Everglades in Florida, plant life decays and subsides, eventually to be covered by silts, sands and other materials. Perhaps millions of years from now, those areas will contain large coal beds. For the use of coal in various purposes, there is a need of widely acceptable classification of coal. The very old and earliest classification was based on the visual observation and the burning characteristics of coal are as follows:

Lignite or brown coal: Brown or Black color woody substances with high moisture contents Bituminous coal: Black in color, easily ignites, and burns with flame and smoke. Anthracite: Black color and lustrous, difficult to ignite and burns without flame. In 1837, Regnault first classified the coal based on chemical composition in five categories on the basis of total oxygen and nitrogen percentage using the ultimate analysis of coal. In 1844, Walter R. Johnson, divided them according to **the ratio of fixed carbon to the volatile matter which is defined as Fuel ratio**. P Frazer (1887) used the fuel ratio to classify the various coals and it was tabulated as

Table 1. Classification of various coals based on fuel ratio

Coal	Fuel Ratio
Dry anthracite	**100-12**
Semi anthracite	**12-8**
Sub-bituminous	**8-5**
Bituminous	**5-0**

The different types of coal are usually classified by rank which depends upon the degree of transformation from the original source (i.e., decayed plants) and is therefore a measure of a coal's age. As the process of progressive transformation took place, the heating value and the fixed carbon content of the coal increased and the amount of volatile matter in the coal decreased. The method of ranking coals used in the United States and Canada was developed by the American Society for Testing and Materials (ASTM) and is based on a number of parameters obtained by various prescribed tests.

The following table (**Table 2**) discusses about different grades of Indian coal, their characteristics and uses.

Table 2. General Classification of Indian Coals (IS : 770-1964)

Type	Name	Symbol	V.M. % at 900±15^{0}C Unit coal basis	Gross Calorific value kcal/kg	Chief uses
Anthracite	Anthracite	A1	3-10	8330 - 8670	Gasification, producers, domestic and where intense

	Semi anthracite	A2	10-15	8440 - 8780	heating and no smoke are required.
Bituminous	Low volatile (caking)	B1	15-20	8670 - 8890	Carbonization for the productions of metallurgical coke
	Medium volatile (caking)	B2	20-32	8440-8780	
	High volatile (caking)	B3	over 32	8280-8610	coking coals, gasification
	High volatile (semi caking)	B4	over 32	8000-8440	Long-flame heating
	High volatile (non caking)	B5	over 32	7500-8060	Steam raising, gasification, long flame heating
Sub-bituminous	Non caking	B6	over 32	6940-7500	Steam raising, Gasification
Lignites or Brown coal	Normal lignite	L1	45-55	6110-6940	Steam raising, briquetting gasification
	Canneloid lignite	L2	55-65	6940-7500	

Analysis of coal is also reported in terms of some arbitrary basis. These are,

1) Run-of-mine (ROM): When the coal directly obtained from a mine is analyzed by elemental or proximate analysis, the data are called run-of-mine.

2) As-received: After extraction from mine, coal is transported to the receiver. The analysis data obtained at this point is called as-received.

3) Air-dried: When analytical data are collected after air drying the coal at a standard condition of 40^0C and 60% relative humidity, the data are called at air-dried basis.

4) Dry: When the effect of moisture content is removed from the analytical data, then that is said as dry basis.

5) Dry and ash-free (**d.a.f**): When the data are reported excluding the effect of ash content, then it is said d.a.f basis.

6) Dry and mineral matter free (d.m.m.f): When effects of both moisture and mineral matter are removed from the analytical data, then it is reported as d.m.m.f basis. This is the data of pure coal only.

7) Moist-mineral-matter-free: This is the basis where the effect of mineral matter is excluded, only pure coal and moisture are taken to report the data.

❖ Carbonization of coal

• Coal preparation and washing

The raw coal extracted out from the coal mine is processed through different techniques to achieve the desired qualities. These result in higher economic value of run of-mine (ROM) coal. The environmental impacts of burning of coal should also to be kept in mind. The mineral matters of the coal should be reduced during its processing such that, the emissions of sulphur dioxide (SO_2), carbon dioxide (CO_2) and particulate matters are minimized during burning. The technology of coal washing or coal preparation is applied to produce specific desirable coal products from the run-of-mine coal without the change of the physical identity. In the early days, the coal in the form of lumps were supplied for domestic use and the intermediate sizes were kept for the industrial use, whereas, the fines were rejected. The sizing facilities were gradually developed. The sophisticated handling and screening facilities were introduced into the market as per customer requirements. Recently, the demand of smaller sized coal has increased. The larger sized coals are kept for their shipment. The washing technique was first introduced in Europe in 1918 and later “Chance” washer was used. The washer utilized sand and water as medium. In course of time, many other types of washing technology have been introduced and then they were modified or rejected according to the need.

- **Coal preparation**

Coal preparation includes blending and homogenization, size reduction, grinding, screening and handling. The most important step is coal beneficiation or cleaning. The cost of coal preparation depends on the methods used and also on the degree of beneficiation required, which is greatly determined by the market demand of the product. Almost all coal used for electric power generation and industrial boilers is either pulverized or crushed and sized before burning. The presence of non-combustible material or ash in run-off-mine coal increases in net heat content but it reduces the dust, ash content, transportation and shipping costs. Ash content also increases wear in coal grinding equipment and boilers. Therefore, coal can be subjected to different levels of cleaning, depending upon its type, its utilization with consideration of the cost of cleaning. Very dirty coals containing large amount of extraneous mineral material, could only match the market specification after substantial cleaning. The final selling price of this coal is determined by the cost of the cleaning steps. The equipment used for washing of coal includes centrifuges, froth flotation devices, disc filters, thickeners, cyclones, and thermal dryers.

❖ Coal preparation process

Typical steps in coal preparation include:

- Crushing
- Screening into different size fractions
- Physical, chemical or mechanical processes to remove undesired impurities
- Dewatering
- Thermal drying
- Blending
- Agglomeration or briquetting

Coal preparation process starts with crushing and screening of freshly mined coal, which removes some of the non-coal material. Mechanical cleaning or “washing” is actually the process of separation of non-coal materials or undesired adherent materials of coal by using a liquid medium. The liquid medium may be an aqueous solution or organic liquid. Sometimes a heavy, finely ground mineral, such as magnetite is added in the liquid medium to ensure the removal of unwanted rock and mineral matter from coal particles. Wet or “hydraulic” cleaning technique is a process which includes agitation of the coal-liquid feed by aeration, materials sorting according to relative density in hydro cyclones, and froth flotation to recover fine coal particles. To meet environmental regulations, modern wash plants are able remove around 40 percent of the inorganic sulfur in coal. A rarely used technique is dry technique in which coal and non-coal materials are segregated by vigorous shaking and pneumatic air-flow separation for crushed feed coal. Dry technique is used before actual washing.

Prepared coal is usually dewatered to some extent as excess moisture lowers the deliverable heat content in the coal and increases the weight of coal. Dewatering equipment includes less costly vibrating screens, filters, or centrifuges to the more costly heated rotary kilns or dryer units.

- **Washing or Cleaning of Coal**

Washing of coal represents the most important step of coal preparation. The raw run-of-mine coal must require some selective qualitative and quantitative analysis for finding out the most suitable operating conditions for cleaning of coal to obtain the desired quality. Among these analyses washability test is most important.

- **Washability Test**

The washability test method can be used to investigate the cleaning characteristics of coarse and fine-coal fractions. However, especially with the fine-coal fractions, this test method may not be applicable for low-rank coals.

Washability characteristics of coal is applied to

(1) Find the relative ease for separation of coal from the refuse based on the difference in specific gravity.

(2) Find the effectiveness of coal washing in particular process.

(3) Characterize the type and amount of impurities

(4) Select the optimum plant operation

(5) Gather the information for designing a separation plant.

The washability test is done by float and sink method. The float and sink test is an important analytical technique for the cleaning of coal in most effective way.

- **Float and Sink Test**

In the float and sink method, the freshly mined coal lumps are first crushed into different size fractions such as, 50-25, 25-13, 13-06, 06-03, 03-0.5 mm through screen analysis. The different fractions of the coal are separated by washing with different specific gravity organic solutions like carbon tetrachloride, perchloro-ethylene, benzene or aqueous solution of zinc chloride or other inorganic salt. Each of the individual size fractions are subjected to sequential float and sink tests with different density liquid. The liquid solutions of varying density with a very small difference in specific gravity such as 0.01 are prepared within the range of 1.25 and 1.9. Sometimes the density range may be broadened upto 2.25 depending on the type of coal. The different size coal samples are immersed into organic solution of known specific gravity, then the float and sink fractions of coal obtained in the washabilty test are separated out. The ash content of each fraction is determined. The float-sink test can be performed on samples ranging in size from bulk samples to bench-scale of coal samples.

By using liquid of different specific gravity the coal samples are divided into number of fractions with increasing order of specific gravity and hence, of ash value. From the results of the test, three curves are plotted.

i) Total float-ash curve

ii) Total sink-ash curve

iii) Washablity characteristic curve or instantaneous ash curve.

By the analysis of plots i) and ii), as shown in **Fig.** 6, the ash content of the clean product (float) and waste material (sink) are obtained by washing with a particular specific gravity of liquid.

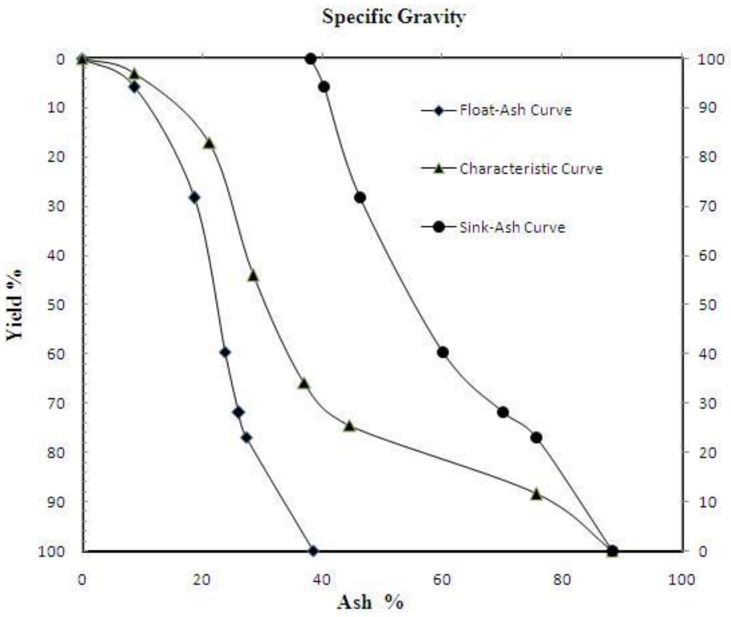


Fig. 6. Characteristic curve of Float and Sink test.

Among the widely used washers, jig washer is one of the important one. In a jig washer, coal is supported on a perforated tray and a continuous periodic flow of water is applied in both upward and downward direction. While washing by this way, clean coal is accumulated in the upper layer of the bed while unwanted heavy non-coal part settles at the bottom. The water may be pulsated by various means.

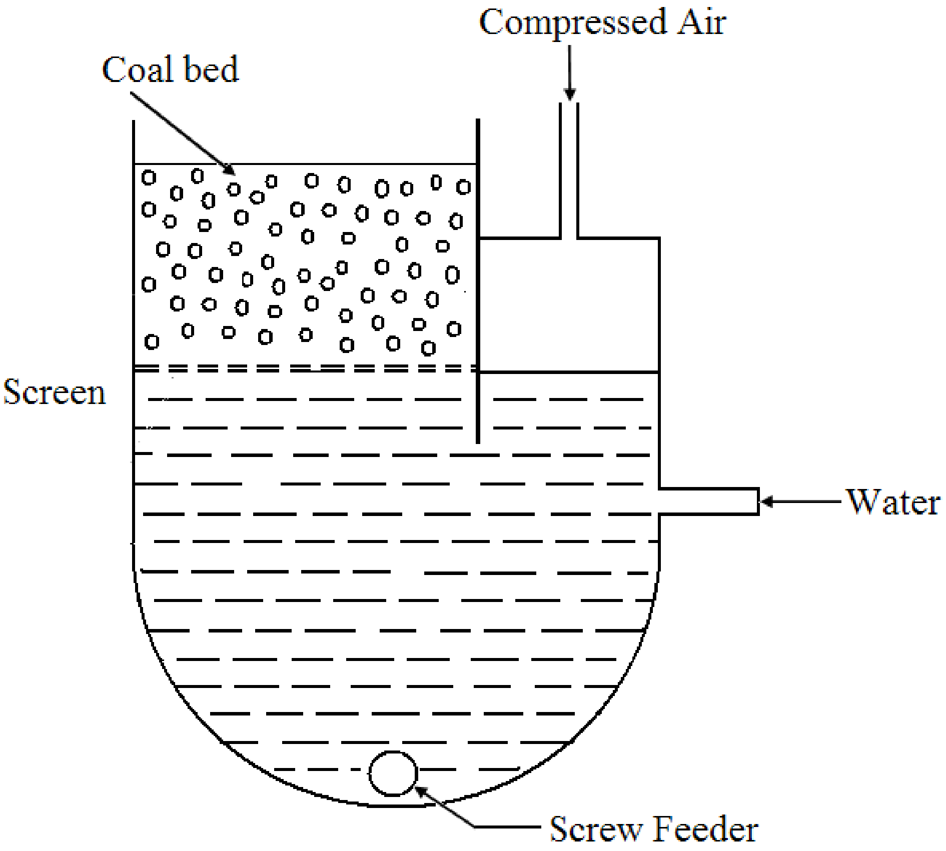


Fig. 7. Baum Jig.

A typical jig washer is shown in **Fig. 7**, which is called Baum jig. It consists of a **U-shaped** chamber, divided vertically by a partition in two parts. One section is washing chamber and another one is air chamber. Feed coal is fed in the washing compartment and compressed air is passed in air compartment for generation of pulse in water. Cleaned coal carried out by the water flow over a weir and the refuse sinks at the bottom. Refuse is removed time to time from the washer.

❖ Combustion of Coal and Coke Making

• Action of heat on different coal samples

Coal can be used in a wide variety of ways, such as, direct burning to produce heat, to generate steam, gasification and liquefaction. In combustion processes, pulverized coal is preferably used, as finely ground coal has more surface area per unit weight than larger particles. Coal is finely ground so that 70 to 80 percent by weight passes through a 200-mesh screen. Coal powder is burned in a combustion chamber in a flow of air. The resulting energy is used to generate steam which is used to turn large turbines and generate electricity. On heating of pulverized coal sample in presence of air, the following changes occur:

1. Loss of entrapped gases inside the coal, such as, methane, ethane, carbon dioxide, nitrogen etc., at or below 100^0C
2. Escape of moisture between 100 to 150^0C
3. Evolution of gaseous products and vapours due to the decomposition of organic components of coal at different temperatures for different coal types.

The decomposition of organic matter of pit and lignite starts at or below 100^0C and of bituminous coal at 200 to 375^0C. Release of volatile matter due to thermal decomposition is termed as devolatilisation. As the coal is heated, the weaker bonds of the coal compounds rupture at lower temperatures and stronger bonds break at higher temperatures. The resulting products of devolatilisation are oxides of carbon, pyrolysis water, hydrocarbons and hydrogen, which are collectively referred to as volatiles. These escape through the solid carbon matrix to the surrounding environment. Except these products, some heavy and highly reactive species, such as tar, may also undergo secondary reactions such as cracking and polymerization. The end products of devolatilisation are carbon-rich residue and hydrogen-rich volatile part than the parent coal.

The chemical changes of coal during heating depend on the type and rank of the coal, rate of heating, maximum or peak temperature of heating, retention time at the highest temperature, pressure, particle size etc. Among the occluded gases in the coal, carbon dioxide and methane are driven off first at 200^0C. Above this temperature, a certain amount of condensation occurs within the coal mass, with the evolution of carbon dioxide and water. The extent of these reactions is more for lower rank of coal. In the temperature range 200-500^0C the organic sulfur compounds of coal decomposes with the evolution of hydrogen sulfide and other organic sulfur compounds.

Along with these, decomposition of the nitrogenous compounds begins to release nitrogen and ammonia. Except these gases, methane and its higher homologous compounds and olefins are formed in this temperature range due to the decomposition of the higher organic coal compounds. Oxygen content of coal is reduced to some extent and appears in the gases evolved mainly as water and oxides of carbon. The evolution of hydrogen usually begins at around 400-500^{0}C. At about 700^{0}C, a sharp and rapid evolution of hydrogen and carbon monoxide occur. In general, as the temperature increases, the release of hydrogen, carbon monoxide, methane and nitrogen increase while higher hydrocarbons decrease. The expulsion of oil vapours from coal starts at about 300-400^{0}C, the yield of tar usually increases to a maximum at 500-600^{0}C. As the temperature increases, the aromatic nature of light oil and tar increases. Thus, the liquids produced from coal at lower temperatures consist mainly of hydroaromatic compounds, small quantities of higher olefins and paraffin hydrocarbons with very little aromatic compounds of the benzene series. Another product, higher temperature tar contains quite high proportions of aromatic hydrocarbons.

When devolatilization is carried out under inert conditions, it is termed as **pyrolysis**. Pyrolysis is of commercial importance in coal liquefaction and in the production of chemicals from coal tar. High temperature devolatilization carried out at above 1200^{0}C, is known as carbonization. Devolatilization in a hydrogen atmosphere is known as hydropyrolysis, which is one of the core reactions in coal gasification processes. In addition to the above, coal can devolatilize in an oxidizing or combusting environment, such as the that present within a combustor as discussed above. Some coal samples on heating exhibit thermoplastic behavior with the formation a highly viscous non-Newtonion liquid after melting. They are referred to as plastic coals or softening coals. After solidification, these coals form 'cakes' and are therefore also called caking coals. The nature of the decomposition products of coal depend on the rank of coal. The degree of aromatization in coal structure increases with the increase in the rank of the coal. Lower and higher rank coals, such as lignite and anthracite, decompose before melting and these are the noncoking and weakly coking coals. Coals of intermediate rank, such as, some verities of bituminous coals are coking. Thus, the primary physical changes which occur on heating a coal sample depend on the differences between the tendencies of the coal to melt and decompose. The process of devolatilization in small particles is found to be isothermal and usually kinetically controlled, if the heating rates are not very high, however, as the particle size increases, the surface to volume ratio decreases and the combustion may become primarily diffusion controlled.

The devolatilization of large particles is significantly different from that of small particles, due to the presence of heat and mass transfer resistances which act in these particles. These resistances not only affect the volatile release rate but also the product yield and distribution. Recently, there has been a considerable interest in understanding the devolatilization behavior of large particles, typically greater than 1 mm as, commercial fluidized-bed coal combustors and gasifies make use of relatively larger particles. The size of the coal particle is one of the important factor for devolatilization time. Usually, longer time is needed for bigger particles to devolatilize than the smaller particles and this is because the heating up of the former particles takes more time than the latter particles. It was found that particles of sizes up to 2.60mm devolatilize in less than 10 sec after they are added in the hot bed.

The hydrogen in coal is used up partly to produce hydrocarbons and water. The heating (calorific) value of coal and char is a significant factor in the conversion of coal to other useful forms of fuel, as well as in its direct use. The heating value of a fuel may be determined either by a calculation from a chemical analysis or by burning a sample in a calorimeter. In the former method the calculation should be based on the ultimate analysis, which gives the account of elementary constituents of carbon, hydrogen, oxygen, nitrogen, sulphur, ash and moisture. A proximate analysis, which determines only the percentage of moisture, fixed carbon, volatile matter and ash, without determining the ultimate composition of the volatile matter, cannot be used for computing the heat of combustion with the same degree of accuracy as an ultimate analysis. The following table shows heating values of some of the coals:

Coal Grade	**Heating value (kJ/kg)**
Anthracite	30080
Bituminous	33412-25047
Sub-bituminous	21319-20830
Lignite	16077

Anthracite has lower volatile matter than bituminous coal, hence the high-volatile variety of bituminous has higher heating value than anthracite coal. Coal is one of the principal potential sources of fuel for energy generation and a valuable raw material for industrial chemicals. But unfortunately, coal contains many impurities like sulfur, nitrogen, sodium, potassium and other toxic impurities. To avoid environmental pollution, the emission levels of these contaminants must be kept as low as possible during combustion.

- ***Combustion of Coal***

Combustion may be defined as the rapid high temperature complicated chemical reaction of oxygen with carbon, hydrogen and sulphur of coal. These reactions follow mainly four steps.

1. Formation of coal-oxygen complexes with evolution of heat.
2. Decomposition of these complexes with the generation of CO_2 and H_2O molecules and formation of carboxyl (COOH), carbonyl (C=O) and phenolic -OH groups along with more heat generation.
3. Decomposition of these groups to produce CO, CO_2, H_2, H_2O and hydrocarbons such as ethane, ethylene, propylene etc.
4. Decomposition of aliphatic structure with the formation of CO, CO_2 and H_2O.

In low temperatures, the first step is developed faster than others. Oxygen molecules are diffused through the pores into the internal surface and are attached to the coal surface by physical adsorption. In this stage, the oxide layer formed due to the exposure of coal surface to the air, prevents the diffusion of oxygen partially and oxidation rate is decreased with time. The reactions between oxygen and coal are exothermic. The reaction rate increases as the temperature increases and as a result coal reaches to ignition temperature at about 175°C with the firing of a flame. The time required from the beginning of oxidation to reach the ignition temperature is called incubation period. Ignition point is the temperature at which the temperature of the combustible material should be reached before it is combined with oxygen and combustion takes place. For complete combustion to take place, sufficient time must be allowed before the temperature of the gases is lowered below that point. In complete combustion, the carbon combines with an equivalent amount of oxygen to form CO_2. Incomplete combustion occurs when coal does not unite according to the reaction stoichiometry. In this type of combustion carbon monoxide, CO, may be formed which may be burned to carbon dioxide by the reaction with more oxygen. The hydrogen and oxygen combine to produce H_2O vapour. Sulphur is converted to SO_2, which in dissolution with water forms sulphuric acid. It is clear that the amount of oxygen required for the combustion of a definite species or compound is fixed. Calorific value of each combustible substance is unique for it.

In practice it is impossible to obtain complete combustion with the theoretical amount of air. In most of the cases, excess, amounting to double or more than the theoretical supply of oxygen is required, depending upon the nature of the fuel to be burned and the method of burning it. The reason for this is that it is impossible to bring each molecule of oxygen in the air into intimate contact with the particles in the fuel that are to be oxidized. It has been shown experimentally that coal usually requires 50 per cent more than the theoretical net calculated amount of air, or about 18 kg per kg of fuel either under natural or forced draft. If less than this amount of air is supplied, the carbon burns to carbon monoxide instead of dioxide and its heat as complete combustion is not obtained. Coal combustion is extensively used for both industrial and domestic purposes. Boilers of power plants, industrial boilers and heat kilns consume most of the world's reserve of coal. Space heating and domestic use is responsible for consumption of a large amount of coal in each year.

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Module-2

Liquid Fossil Fuel (Petroleum)

❖ History of liquid fuel

Petroleum is the naturally occurring liquid fuel and it accounts for the bulk of the liquid fuels. Petroleum can be defined as a mixture of gaseous, liquid and solid hydrocarbons or hydrocarbon derivatives that occur naturally within the geological traps. It is generally agreed that petroleum was formed by processes similar to those which yielded coal, but was derived from small animals, mainly marine animals, rather than plants. Dead organisms have been buried in mud over millions of years. Further layers deposited over these mud layers, may reach a thickness of thousands of feet. When a layer was particularly rich in broken sea shells, it was compacted into limestone. Sandy layers become sandstone. The bodies of the organisms in the mud layer were decomposed by high temperature and pressure of the earth layer and converted to fatty liquids and solids. Heating these fatty materials over a very long time caused their molecules to break into smaller fragments and recombine into larger ones. Hence a wide range of molecular size found in crude petroleum was obtained by this process. Bacteria were usually present and helped to remove oxygen from the molecule, which were mostly carbohydrates, comprising of carbon, hydrogen and oxygen. These carbohydrate molecules were turned into hydrocarbons by the bacterial action. High pressure of the overlying rock layers forced the oil to migrate from compacted mud layer (shale) to less compacted limestone, dolomite, sandstone layers. The first type of rocks (sedimentary rocks) has lesser permeability than the second type (reservoir rocks). During this migration, the composition of oil may be changed due to filtration, adsorption etc.

❖ Accumulation of petroleum in sediments

Reservoir rock must possess fluid holding capacity and also fluid transmitting capacity. Most reservoir rocks are coarser grained sedimentary rocks. Cap rock act as a seal to prevent the escape of oil and gas from the reservoir rock. Typical cap rocks are clays and shells, rocks in which the pores are very much finer than those of reservoir rock. It also has far lower permeability than reservoir rock. Salts, anhydrites, gypsum which are called evaporates also act as cap rock. In the following the diagram (**Fig.** 8.) a probable accumulation pattern of gas, oil and brine water under the earth is described.

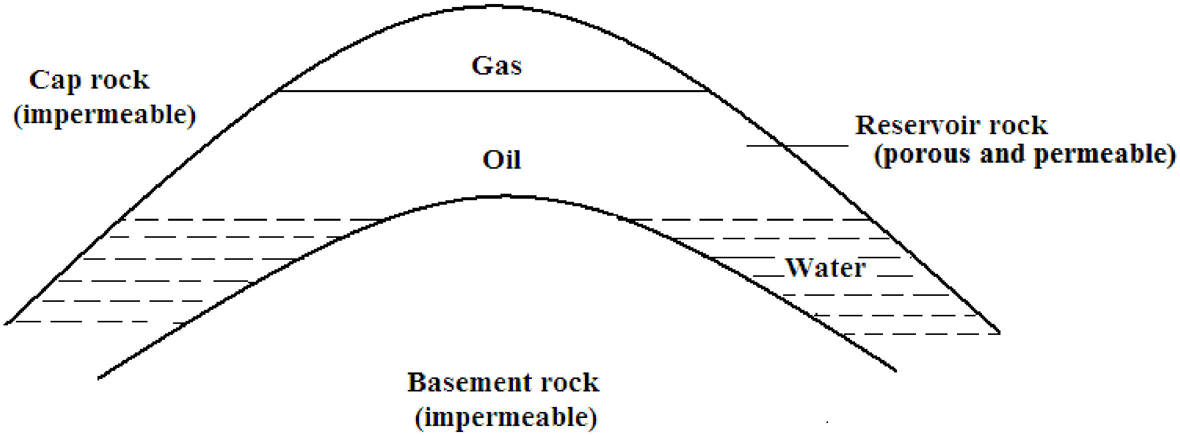


Fig. 8. Accumulation of gas, oil and water in a dome-shaped reservoir rock

Once formed, the sedimentary rocks are subjected to various kinds of deformation, such as folding and faulting. Anticlines are upfolds in layered rocks, which are important type of structural traps in petroleum geology. Circular upfolds in the rocks are called “domes”. Synclines are the opposite of anticlines, which are downfolds, usually occur between two anticlines. More or less circular depressions in the layered rocks are called “basins”. Both these folds may extend from feets to miles long. Faults are breaks or fractures in rocks along which one side is moved relative to other side. Fauting is important for entrapment and migration of oil at some places. The distribution of fluids in a reservoir rock is dependent on densities of the fluids and the detailed capillary properties of the rock. Taking the simplest case of a rock in which pores are uniform size and evenly distributed, the fluids are distributed in the order, gas, oil, brine water in the ascending order of density. The upper zone of the rock pores are filled mainly by gas (gas cap), a middle zone, which is occupied mainly by oil with gas in solution and a lower zone, filled by water. Usually, the gas-oil and oil-water contact is horizontal, but there are cases where these are inclined.

- **Composition of petroleum**

Petroleum is not a uniform material. Its composition can vary with the location, age and also individual well. On a molecular basis, petroleum is a complex mixture of hydrocarbons and organic compounds of sulfur, oxygen and nitrogen, as well as compounds containing metallic constituents, particularly vanadium, nickel, iron and copper. The hydrocarbon content may be as high as 97%, for example, in the light paraffinic petroleum or as low as 50% or less as illustrated by heavier asphaltic crude oils.

- **Exploration of crude petroleum**

It has already been discussed how liquid petroleum is originated and formed within the sedimentary rocks under the earth. These rocks make a source of reserve of crude petroleum. The sedimentary rocks which have commercial value in terms of exploration, are important. These are also called reservoir rocks. The structures of reservoir rocks are of different types, such as, anticline, syncline, folds, faults, fractures, unconformities etc. The two essential properties of reservoir rock are porosity and permeability. Porosity is the storage capacity of the rock. This is sometimes expressed as porosity (%-void ratio) as:

$$Porosity(\%) = \frac{void\,volume}{rock\,volume} \times 100$$

Permeability is the rate of flow of fluid through the rock. It is expressed by Darcy's law which states that the rate of flow of a homogeneous fluid in a porous medium is proportional to the pressure gradient and inversely proportional to the fluid viscosity. Permeability is expressed in **Darcies (D)**. As most of the petroleum reservoirs have permeability less than 1D, hence **millidarcy** (1/1000 D) is usually used.

For petroleum oil exploration, the knowledge of underground structures is necessary. In this respect, the data about the properties of subsurface rocks in those structures should be acquired. The properties which are encountered in gaining the data are density, elasticity, magnetic and electrical properties of rocks. All these data collectively gives the idea of occurrence and commercial exploration of crude petroleum at a definite reserve. The principle of obtaining those data mainly depends on the use of magnetism, gravity and sound waves and the respective instruments used are, magnetometer, gravimeter and seismograph.

Magnetometer is a specially designed instrument which can detect minute differences in the magnetic properties of various rock structures, which helps to find out the formations that might contain oil. Except this, magnetometer provides the clue about the depth of basement rock, the probability of finding the locations which may have anticlines or other oil-favourable structures. Gravimeter detects differences in the gravity pull between the normal gravity and the gravity of a subsurface structural formation. This gives the indication of the location and density of underground rock formations.

Seismograph works on measuring the shock waves obtained from explosions initiated by triggering small controlled charges of explosions in the bottom of the shallow holes in the ground. Usually a series of detectors is placed in a predetermined fashion around the location of the explosion. The acoustic waves travel outwardly in all directions and some are reflected back to the ground surface by denser rock formations below. The formation depth is determined by measuring the time elapsed between the explosion and detection of the reflected wave at the surface. Seismic geophysical work is also done on the water. A marine seismic project moves continuously with detectors at a definite speed and at a definite depth. The detectors are towed behind the boat. Explosives are charged at a position and time, determined by the speed of the boat and the reflections are continuously detected at every position of the water level. Another important exploration process is borehole logging. In this method a well is drilled and various instruments are employed to log or acquire data at different positions of the well in terms of the properties of the rocks, such as, electrical resistivity, radioactivity, acoustic or density.

- **Drilling operation**

Drilling oil and gas well is a complicated and very expensive operation which needs the knowledge of many aspects of engineering and geosciences. The exploration and drilling processes are planned in such a way so that the whole process becomes safe and cost-effective. Oil and gas reservoirs are found in a variety of geographical areas. The wells drilled in these reservoirs may be onshore or offshore. The depth of the well may vary from 1000 to 30,000 ft and wells may be drilled either totally vertically or in many cases a larger part of the well may be drilled in inclined or horizontal manner. Most of the drilling operation is done by rotary method in which an abrasive bit is revolved at the end of a drilling stem or drill string. Generally, almost all drilling rigs (the assembly which is used for drilling) are composed of the components: a power plant, hoisting and rotary machinery, the drill column, a mud circulation system and auxiliaries. The power used for drilling may vary from 250 to 2000 bhp, a heavy duty mud pump needs around 700 bhp. Hoisting system is a large pulley system which is used to run and pull the equipments (drill string and casing) into and out of the well. Rotary system is used to rotate the drill string and therefore the drill bit, on the bottom of the borehole. Completing a well and preparing for production of oil involves insertion of a casing which comprises of one or more strings of tubing. The casing provides a permanent wall to the borehole, prevents cave-in, blocks off unwanted water, oil or gas from another formation, provides a return passage for the mud stream and provides control of the well during production. The mud circulating

system is used to circulate the drilling fluid or mud down the drill string, up the drill string to the borehole annulus and for carrying the drill cuttings from the mouth of the bit to the surface. Drilling fluid is usually a mixture of water, clay (bentonite), weighing material (barite) and chemicals.
The mud is mixed and conditioned in the mud pits and then circulated downhole by large pumps.

- **The major functions of drilling fluid are**

1. To cool and lubricate the drilling bit and the drill string.
2. To remove drilled solids, allowing their release at the surface.
3. To form a gel to suspend drilled cuttings and any weighing materials, when the fluid column is static.
4. To control subsurface pressure.
5. To prevent squeezing or caving of formations and to plaster the sides of the borehole.

Mud is pumped through the mud pumps to the top of the drill string and mud then goes through the string to the bottom. At the bottom, mud passes through the bit and then up the annulus, carrying the drill cuttings to the surface. Before mud enters to the mud pit, the solids are removed from it by vibrating screens. Recovery of oil when a well is first opened is generally by natural flow, forced by the pressure of the gas or fluids that are contained within the reservoir. At the beginning, there may be a chance of flush, hence at this stage, well should be carefully controlled. There are several ways which serve to drive out the petroleum fluids from the formation to the surface, through the well. These drives are classified as either natural flow (Primary recovery) or applied flow (Improved oil recovery).

- **Natural drive or Primary recovery**

Petroleum is propelled out of the reservoir through the well by one of the three methods, or combinations of those, a) **dissolved gas drive**, b) **gas-cap drive**, c) **water drive**. In dissolved gas drive, the gas dissolved in petroleum oil exerts force to propel the oil as it tends to come out of the solution because of the release of pressure at the point of drilling. Dissolved gas drive is the least efficient method of natural drive as it is difficult to control the gas-oil ratio, rapid drop in the bottom hole pressure and the recovery may be less than 20%. If there is a gas cap above the oil reserve, then this compressed gas is utilized to drive the oil into the well. This is gas-cap drive. Normally the gas-cap contains methane and other hydrocarbon gases, which may be separated from the oil after the recovery, by compressing the gas. Natural gasoline is a well-known example of the recovered compressed hydrocarbon, which was formerly known as casing-head gasoline or natural gas-gasoline. The normal percentage recovery in a gas cap drive is 40 to 50%.

Water drive is the most efficient method of natural drive where the propulsive force comes from the water accumulated under the oil. Water forces the lighter recoverable oil out of the reservoir into the well. In water drive, rate of removal should be adjusted properly so that water moves up evenly through the hole. The recovery in a properly operated water drive may be as high as 80%.

- **Improved oil recovery (IOR)**

IOR is any activity which increases the recovery above that of the primary recovery. It may include drilling extra wells or drilling horizontal wells, which intersect the reservoir areas which may otherwise be missed. IOR may also be done by supplying energy to the reservoir. IOR can be done by the two broad ways, secondary recovery and enhanced oil recovery. Secondary recovery involves adding external energy without making any fundamental changes to the physical properties of the fluids. This energy is added either by water or gas injection. The secondary gas or water injection mimic the naturally occurring processes of solution gas drive and water drive respectively. Enhanced oil recovery which is sometimes known as tertiary recovery involves adding external energy and creating fundamental changes to the physicochemical properties of the system. The addition of external energy is in the form of using chemicals or heat to the reservoir to effect changes in fluid density, viscosity, interfacial forces or to change the wettability which affects the distribution of the oil, gas and water within the pores.

- **Evaluation of crude**

The assessment of a crude oil mainly involves the chemical evaluation of crude oil feedstocks by petroleum testing laboratories. Each crude oil type has unique characteristics and no crude oil is identical to the other. The results of crude oil assay testing provide extensive and detailed analytical data for a particular crude oil which are necessary for refinery. In practice it is difficult and very expensive to carry out full laboratory analysis of every type of crude oil at the refinery. This has resulted in development of a number of computing methods that can predict the properties of petroleum fractions by routine laboratory analyses. For application of these methods, information about distillation characteristics, density, sulfur content, viscosity etc. of petroleum fractions are required.

According to U.S Bureau of Mines, eight bases of crude oil are designated depending on the distillation characteristics. The characteristics of a crude oil is expressed according to key fraction no. 1, which boils at 482 to 527^{0}F at atmospheric pressure and key fraction no. 2, which boils at 527 to 572^{0}F at 40 mm pressure in a standard example distillation apparatus and condition. **Table 3** shows different crude oil bases with their characterization factors and API gravity. The bases of the crude oil are designated as paraffin, paraffin-intermediate, paraffinnaphthene etc, depending on the nature of the low boiling and high boiling fractions of crude. For example, in paraffin-naphthene base, the first word of the base name, such as 'paraffin' denotes the nature of the low boiling fraction and the second word, 'naphthene' indicates the nature of the higher boiling fraction of the crude oil.

Characterisation factor of a crude oil, defined by **Universal Oil Product (U.O.P)** is expressed as

$$K = \frac{\sqrt[3]{T_B}}{S}$$

Where, K is the characterization factor, T_B is the molal average boiling point in ^oR and S is the specific gravity at 60^{0}F. Bases of crude oil can be indicated primarily by this factor. Paraffin base crude oils show the range of characterization factor as 12.9 to 12.15, for intermediate base crude oils the range is 12.1 to 11.5 and for naphthene base crude oil it is 11.45 to 10.5. These ranges are determined based on the properties of crude oil, such as, viscosity, aniline point, molecular weight, critical temperature, percentage of hydrocarbon etc.

Table 3. Different bases of crude oil with their properties

Base of crude oil	API gravity at 60^0 F		Approx. U.O.P characterization factor	
Low boiling part High boiling part	Key fraction 1	Key fraction 2	Low boiling	High boiling
Paraffin	40+	30+	12.2 +	12.2 +
Paraffin Intermediate	40+	20 to 30	12.2 +	11.4 to 12.0
Paraffin Naphthene	40+	20-	12.2 +	11.4-
Intermediate Paraffin	33 to 40	30+	11.5 to12.0	12.2+
Intermediate	33 to 40	20 to 30	11.4 to12.1	11.4 to 12.1
Intermediate Naphthene	33 to 40	20-	11.4 to12.1	11.4-
Naphthene Intermediate	33-	20 to 30	11.5-	11.4 to 12.1
Naphthene Paraffin	33-	30+	11.5-	12.2+
Naphthene	33-	20-	11.4-	11.4-

A **crude oil** is termed as ‘sour’ crude when it contains dissolved hydrogen sulfide in it, 0.05 cu ft of hydrogen sulfide per 100 gallon of crude oil. At this level, the crude oil becomes dangerously toxic. The crude oils which contain disulfides, mercaptans, thiophenes in a sufficient amount, are said to be ‘high sulfur’ crude. Sometimes ‘high sulfur’ crude oils are erroneously termed as sour crude. Such as, high sulfur crude oils of California, Venezuela and Mexico do not contain any dissolved hydrogen sulfide in them; hence they should not be termed as sour crude. The vaporization characteristics of petroleum mixtures are determined by a batch distillation curve where percentage distilled is plotted against respective temperature at which it is distilled. Theoretically, a true boiling point (TBP) distillation is that where a very close separation is made so that each component in the mixture is separated at its own boiling point and the quantity present in the original mixture. **Fig.9** represents the TBP curve of a mixture containing two components A and B which are present in the volume percent 30 and 70 respectively and their boiling points are t_A and t_B respectively ($t_A < t_B$).

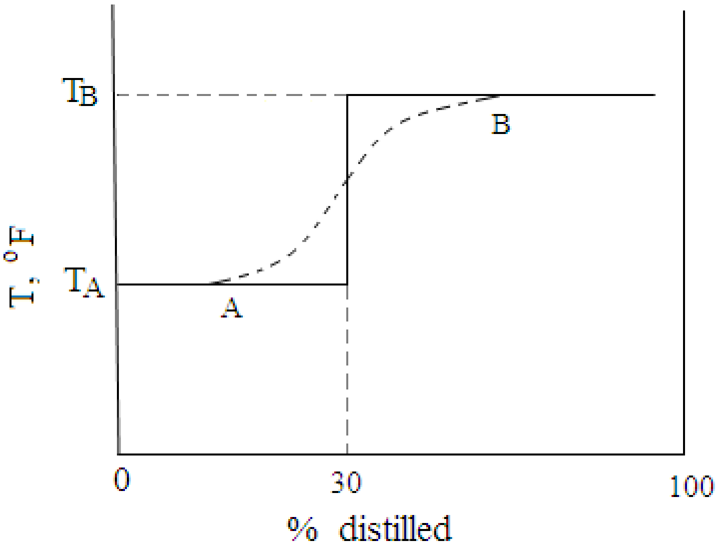
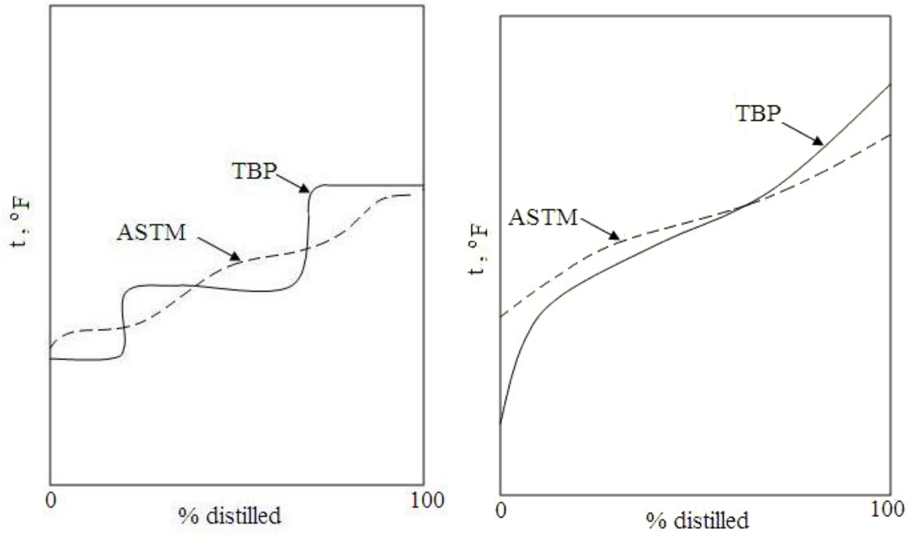


Fig.9. True boiling point (TBP) distillation of a two component mixture

The stepwise plot shows the theoretical **TBP** plot with perfect fractionation while smooth curve represents the actual curve with imperfect fractionation i.e., incomplete separation of the two components. Vaporisation characteristics of petroleum fractions are determined by means of a simple distillation with a little fractionation. This distillation is done by following the methods and apparatus designated by **ASTM** (American Society for Testing and Materials). This type of distillation is called ASTM distillation and the method of this distillation is termed as '**ASTM D158**' in **ASTM** standard. In this method 100 or 200 ml sample is distilled in a batch mode in specified condition and apparatus. **Fig.10** a and b show typical **ASTM** distillation curve for three components compared to the typical **TBP** curve for the same three components and the same curve for a complex system respectively.



(a) (b)

Fig.10. (a) Comparison of **TBP** and **ASTM** distillation curves for a three component mixture (b) for a complex system

Equilibrium flash vaporization (**EFV**) is a type of separation of components of a petroleum mixture where, the mixture under pressure is suddenly vaporized or flashed in a still and the mixture is separated into a vapour and a liquid portion which remain at equilibrium. In fact, this type of flash is observed in the refinery when crude oil containing appreciable amount of light components under pressure is piped to separators at lower pressure and allowed to vaporize suddenly through a pressure reducing valve. If a number of samples of the same composition are flashed at the same pressure but at different temperatures between the bubble point and dew point temperatures of the feed, an **EFV** curve can be generated. Following **Fig.11** shows the comparison of the slopes of **TBP**, **ASTM** and **EFV**. It has been shown that 10- 70% slope of **EFV**> 10-70% slope of **ASTM**> 10-70% slope of **TBP**.

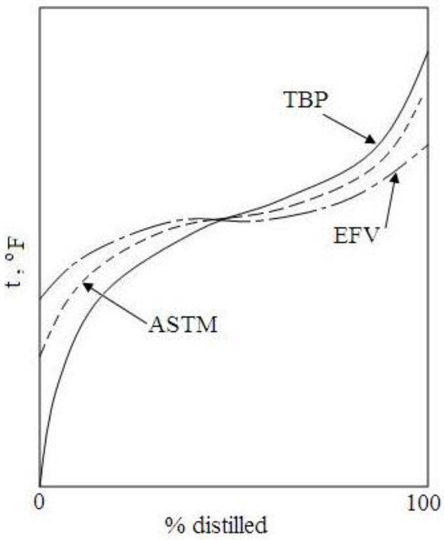


Fig.11. Comparison of the slopes of **TBP**, **ASTM** and **EFV** distillation curves.

The physical properties of petroleum oil vary gradually throughout the range of compounds by which the oil is constituted. Distillation is a means of arranging these compounds in accordance to their boiling points. The properties such as, viscosity, specific gravity, colour etc. are found to vary at each drop or fraction of the mixture distilled. The rate at which these properties change can be shown by mid-percent curve. Actually, the viscosity or specific gravity of a petroleum fraction is an average of that property of many drops which constitute the fraction. The concept of mid-percent curve is that, if each drop is equally different from the last drop and it’s succeeding one, then the property of the whole fraction is determined by the property of the drop which comes at exactly 50% distilled. This would be the condition when a mid-percent curve is a straight line. Although mid-percent curves are never exactly straight line, but they may be straight for a short range of percent distilled and this short range, the average property of the fraction is exactly the same as that of mid-percent fraction. There are some properties which are not additive, such as, viscosity, **API** gravity, colour, flash point etc., for which this mid-percent curve is not suitable. But the properties which are additive, such as, specific gravity, aniline point, percent sulfur etc. can be utilized nicely in mid-percent curve to determine the average property of the whole fraction. Although viscosity is not an additive property, but it has been seen that, for a wide fraction of oil, the average viscosity is almost exactly the same as that of the mid-point fraction.

- **Distillation**

Crude oil is converted to saleable products by combination of physical and chemical processes, collectively known as refining of petroleum. Petroleum refining starts with crude oil distillation which is a physical separation process, followed by some chemical treatment steps, such as cracking, reforming, hydrotreating etc. to produce a wide range of petroleum products of specific standard. Crude oil distillation is done at atmospheric pressure as well as under vacuum. The capacity of a refinery is mostly determined by the capacity of atmospheric distillation unit. A crude oil desalter is considered to be one of the facilities of atmospheric distillation unit. Crude oil is first processed by desalter to remove salts, solids and water before introduction to the atmospheric distillation unit. Desalted crude is then fractionated into intermediate petroleum products or cuts, such as, light naphtha, heavy naphtha, kerosene, gasoil and atmospheric residue (**AR**). Atmospheric distillation produces cuts which boils upto **350^0C**. The whole or part of AR is treated in vacuum distillation unit to produce either vacuum gas oil (**VGO**) or lubricating oil depending on the type of the crude oil and vacuum residue (**VR**). The vacuum distillation unit used for production of **VGO** is called a fuel-type unit and the unit used for producing lubricating oil is said to be a lube-type unit.

- **Atmospheric distillation**

The atmospheric distillation unit consists of a desalter, an atmospheric tower, three side strippers and a debutanizer/splitter. Crude oil is preheated and then sent to desalter. Crude oil contains contaminants such as, salts, solids and water that may cause corrosion, fouling, plugging and catalyst degradation in the refinery units. The salts contained in crude are mainly NaCl, $CaCl_2$, $MgCl_2$ and they are soluble in the water associated with crude oil. This solution forms water-in-oil emulsion which is broken by applying high voltage electrostatic force. In the desalter, the salt containing water forms large drops, which coalesces and then settles by gravity. The desalted crude oil is then removed from the top of the vessel while effluent water is removed from the bottom. From the desalter, the crude oil is preheated by exchanging heat with products and pump around reflux streams and then heated by a pipe-still heater to a desired temperature of around **325^0C**. At this temperature, the required degree of vaporization of crude occurs and then it is introduced into the flash zone of atmospheric tower. The liquid portion of the crude flows down to the bottom stripping section of the tower where the vapour portion or distillate portion are vaporized with steam stripping. Steam is injected at the bottom of the tower which strips out the distillate fractions from the crude and ascends through the column along with the stripped vapour and the flashed vapour from the crude at the time of injection. This mixed vapour steam comes in contact with the down-flowing internal reflux liquid on the trays where mass transfer of the components occur by condensation and vaporization and this way fractionation takes place. The internal reflux is created by condensing a portion of the ascending vapour by exchanging heat with the pump-around reflux liquid. Pump-around refluxes at different point of the tower at different temperatures are utilized for effective fractionation. The condensed liquids are withdrawn at different side-trays as distillate products, such as, kerosene, light gas-oil and heavy gas-oil and the bottom product is recovered as atmospheric residue. The overhead vapour of the tower is condensed by overhead condenser(s). This condensed liquid is called full boiling range

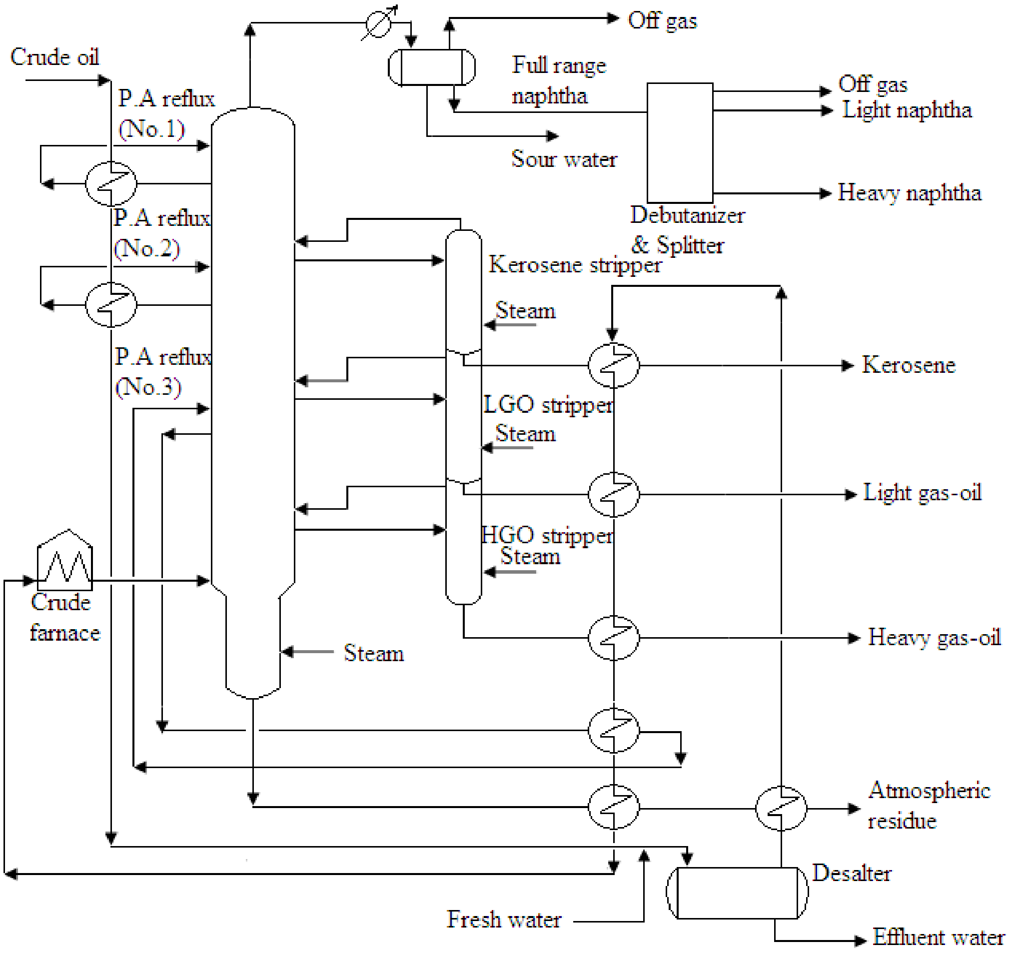


Fig.12. Flow diagram of atmospheric distillation unit

naphtha which is sent to a debutanizer to remove butane and lighter gas. The gases which are not condensed in condenser and the debutanizer are taken out and sent to a gas separation unit to collect gases like, methane, ethane, ethylene, propane, propylene, butane and butylenes. These gases have definite use, such as, propane and butane constitute **Liquefied Petroleum Gas (LPG)**, methane and ethane are used as fuel and preparation of valuable chemicals, ethylene is the feedstock for first generation petrochemicals. The process flow diagram of an atmospheric distillation unit is shown in above **Fig.12**. Before being introduced into the atmospheric tower, crude oil is heated in a crude furnace, named pipe-still heater. Most crude oil starts cracking or decomposition in the temperature range **340-370^{0}C**. Hence, the coil outlet temperature of the furnace should be selected in such a way so as to avoid excessive thermal decomposition, which results in coking in the furnace tube and poor quality and quantity of fractionated products. The typical furnace coil outlet temperature is maintained in the range **310-370^{0}C** depending on the nature of the crude oil.

The full range naphtha withdrawn from overhead of the tower is stabilized in debutanizer (stabilization means removal of light gas components from naphtha to maintain a definite vapour pressure of it) and then sent to a splitter. In splitter, naphtha is separated into light naphtha and heavy naphtha. As an alternative to use splitter, light naphtha and heavy naphtha can be withdrawn as an overhead product and a side cut respectively from top of the atmospheric tower. Kerosene, gas oils and **atmospheric residue (AR)** are obtained as the side cut from the tower. Kerosene, light gas oil and heavy gas oil are steam stripped to remove the light ends and stabilize the product. All these cuts and AR are collected after exchanging heat with the feed. Steam is introduced at the bottom of the distillation tower and to the side strippers to recover the lighter fractions from the liquid stream or product. The rate of steam supplied is usually in the range of 10-50 kg/m^3. If heavy naphtha is withdrawn as side stream product, then a reboiler is equipped with the stripper instead of introducing steam into it. There are generally two types of reflux systems used in the atmospheric distillation. One is a pump-around reflux system and another is overhead reflux system. In the case of pump around reflux system, some of the ascending vapour is condensed at the top part of the tower by exchanging heat with pump around reflux liquid and the condensed liquid flows down the column as internal reflux. In the overhead reflux system, the overhead vapours are condensed and this condensed liquid is sent back to the top section of the column as reflux. Overhead reflux system may be again divided into two kinds, cold reflux and hot reflux. In cold reflux system, vapour from the overhead of the tower is condensed by a condenser and then enters to an overhead reflux drum, where oil, water and gases are separated. A part of the condensed oil is sent back to the top of the column as reflux and the remaining part is collected as naphtha product. For hot reflux system, two sets of overhead condenser and reflux drums are used in series. In the first condenser, heavier fraction of the overhead vapours are condensed and sent to the first reflux drum. The lighter part goes to the second condenser, condensed and collected in the second drum. The condensed liquid which is accumulated in the first drum is sent back to the top of the tower as reflux. As the temperature of this reflux liquid is more than that of the cold reflux liquid, hence, the system is called hot reflux. Cold reflux is comparatively simple in operation, but hot reflux reduces the corrosion in the tower top. For both the cases, the diameter of the tower top is smaller than that for pump around reflux.

- **Vacuum Distillation**

Atmospheric residue (AR) from atmospheric distillation tower contains several valuable cuts which should be recovered. **AR** cannot be fractionated at atmospheric tower as fractionation of this cut needs excessive temperature where, cracking or decomposition of crude starts resulting in severe coke deposition. Hence, **AR** is recovered as a bottom product from the tower and distilled under sub-atmospheric pressure.

Crude oil can be categorized as lube-bearing crude and non-lube bearing crude. Non-lube bearing crude cannot produce lubricating oil cut in vacuum distillation as this range of hydrocarbons are not present in non-lube bearing crude. The unit for processing of non-lube bearing crude and lube-bearing crude are known as fuel-type and lube-type vacuum distillation column respectively. The former produces vacuum gas oil (**VGO**) and later produces lubricating oil as the main distillate product. **AR** is introduced into the vacuum distillation column after heat exchanging with distillation products, vacuum residue and pump-around reflux streams and finally heated in a furnace at required temperature. Vacuum distillation furnace may be classified into two types, wet and dry. In wet type, steam is injected into the furnace coils and that helps to lower the partial pressure of feed as well as steam carries the feed vapours through the furnace tube more rapidly. In dry type, steam injection is not done in the furnace. Steam injection lowers the steam consumption in the vacuum ejector systems. The choice of the type depends on the overall economy of the refinery.

In a fuel type distillation, shown in **Fig.13**, **AR** is flashed at the required temperature in the vacuum tower feed plate. The liquid portion of the flashed feed flows downward in the stripping section and the vaporized part along with stripping steam goes up through the column. Light vacuum gas oil (**LVGO**) and heavy vacuum gas oil (**HVGO**) is withdrawn from the side trays at their respective boiling ranges. These two cuts may be collected together as per requirement. Vacuum residue (**VR**) is withdrawn from the bottom of the tower, after the **VGO** portions are steam stripped. **VR** should have required penetration index (This is a property of bitumen/**VR**, penetration of a bituminous material is the distance in tenths of mm, that a standard needle would penetrate vertically, into a sample of the material under standard conditions of temperature, load and time). A small part of the cold **VR** is recycled at the bottom of the tower to prevent coking. The vacuum tower can be divided into stripping section, wash oil section, **HVGO** section and **LVGO** section, from bottom to top, according to its product draw and working manner. Stripping section is the bottom part of the distillation tower below feed plate, where stripping steam is introduced. A mixture of the flashed vapour, stripped vapour from feed and steam flow up the column and enter into the wash oil section. At this section, this mixture comes in contact with internal reflux stream when any heavy oil fraction entrained in that vapour mixture is taken away by the reflux and lighter fraction from reflux comes in the up-flow stream. This internal reflux is called wash oil.

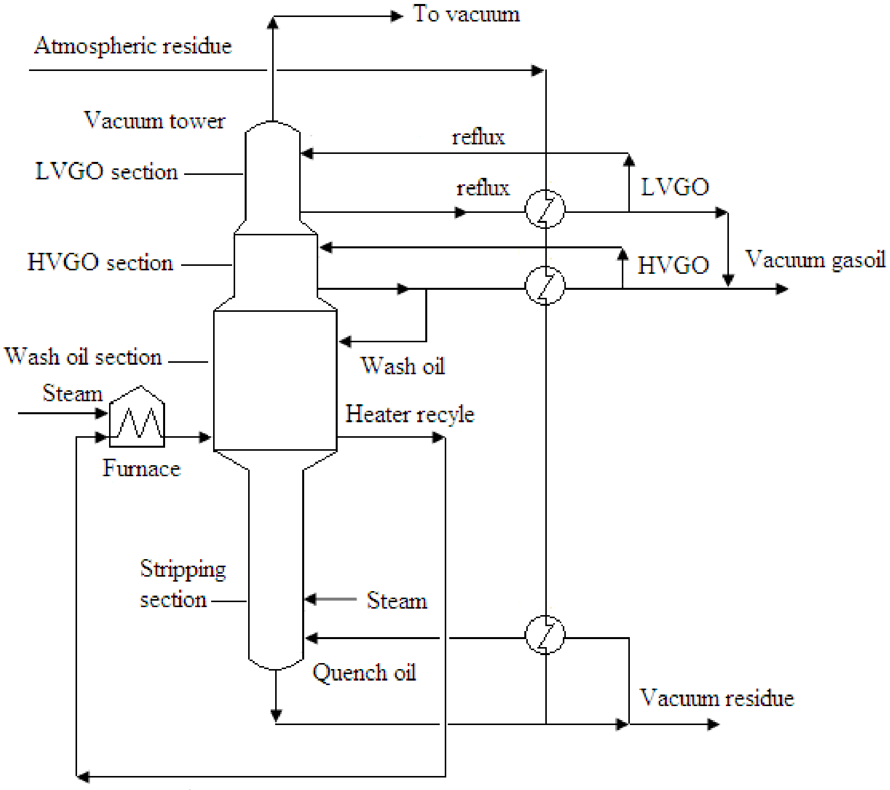


Fig.13. Fuel-type vacuum distillation unit

The washed vapour stream goes up to the **HVGO** section and then to **LVGO** section. **HVGO** and **LVGO** cuts are obtained from side draw trays by contacting with down-flow reflux liquid. The internal reflux liquid is achieved by condensing the ascending vapour by cold pump-around reflux stream. **HVGO** and **LVGO** obtained after condensation from their respective trays and withdrawn as **VGO** product, either separately or together. A part of the wash oil from wash oil section is withdrawn as side stream. This oil containing some fraction of heavy oil is recycled to vacuum tower by mixing with the feed stream before heading to the furnace. The overhead vapour of the vacuum tower, which is the mixture of steam and oil vapour, is pre-condensed to remove most of the steam and oil. The uncondensed part is sent to the ejector system. Vacuum is created by using a series of ejectors and surface condensers. The condensed overhead vapour and steam from pre-condenser and surface condensers are sent to an overhead drum, where gas, slop oil and sour water were separated. In fuels-type vacuum distillation column, no side strippers are employed, as **VGO** is the only side product obtained, whose properties are mainly controlled by its metal content and carbon residue.

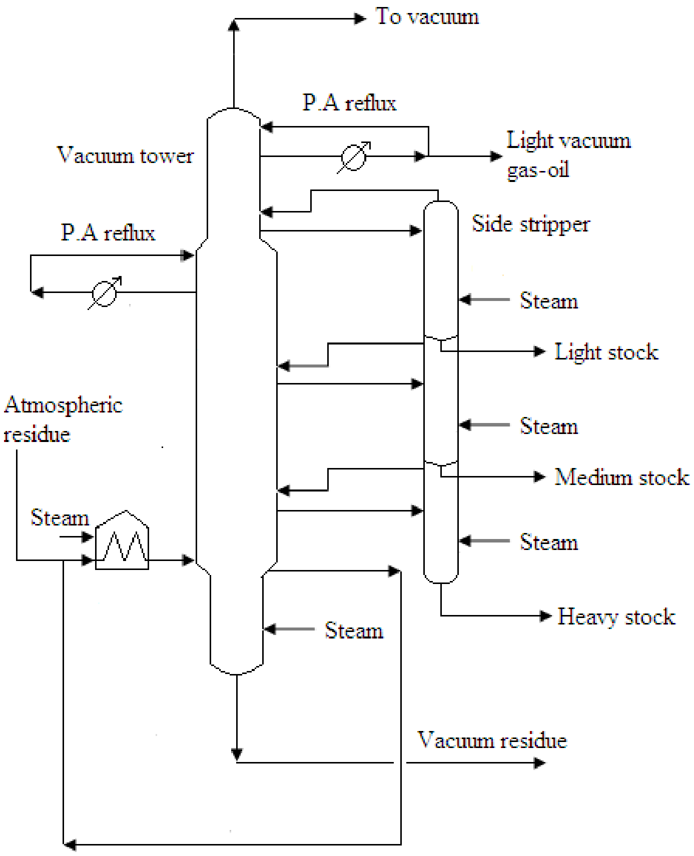


Fig.14. Lube-type vacuum distillation unit

The lube-type vacuum tower is shown in **Fig.14** above. This type of distillation column produces lube-oil base stock as the side stream, **LVGO** as the top product and **VR** as the bottom product. Three types of lube-oil base stocks are withdrawn from three side draw trays, as light stock, medium stock and heavy stock, which are all steam stripped in a side stripper to meet the viscosity and carbon residue requirements of the stocks. Pump-around reflux is used to provide internal refluxes. Steam is introduced at the bottom for stripping the feed liquid. Bubble-cap trays are normally used in this type of distillation column.

The maximum allowable temperature of feed (**AR**) is determined by the type of feed to prevent the cracking and coke formation in the furnace coils. Usually, the maximum temperature is kept in the range of **400-430^{0}C**. The pressure at the tower top is maintained in the range 1.3 to 20 kPa. The overall pressure varies depending on the type of furnace operation (wet or dry), feed temperature and cut point temperature difference between **VGO** and **VR**.

❖ Secondary processing

• Cracking

Cracking is a secondary process in the refinery where change in composition of the petroleum fractions is done by the action of heat alone (thermal cracking) or heat in presence of a catalyst (catalytic cracking). Cracking is the decomposition of **C-C** bond of hydrocarbon molecules. The primary or first stage products of cracking are lower molecular weight compounds than the feed and are mainly olefinic in nature. The second stage products come from the reactions like isomerization, cyclisation, polymerization etc. of primary products in-situ. These secondary products may be of the same molecular weight or higher than the feedstock. The fundamental difference between thermal cracking and catalytic cracking is that, the former proceeds via free radical mechanism while the latter occurs mainly by a carbocation mechanism. Hydrocracking is the cracking operation where hydrogen is introduced during cracking; hence it is a combination of hydrogenation and cracking.

• Thermal cracking

Thermal cracking was first commercialized in 1912 to increase the yield of middle distillate fractions (which boil in the range of **150-350^{0}C**) from crude oil. Visbreaking is a mild thermal cracking operation which improves the viscosity of a heavy fraction (boiling range >**250^{0}C**) by a non-severe route. Coking is a severe thermal cracking operation whose target is to maximize coke production from a heavy stock along with gas, gasoline and middle distillate. Although thermal cracking is not practiced in most modern refinery and is replaced by catalytic cracking yet there is some importance of thermal cracking depending on the products required or aimed.

Following **Table 4** shows the thermal cracking temperature range and the corresponding products obtained thereof.

- **Table 4 Thermal cracking processes**

Cracking temperature (^{0}C)	**Name of the process**	**Products**
425-460	Visbreaking	Fuel oil
460-520	Thermal cracking	Gas, gasoline, fuel oil
520-600	Low temperature coking	Gas, gasoline, soft coke
600-800	Gas production	Gas and unsaturated
800-1000	High temperature coking	Gas, heavy aromatics, pitch, coke
Above 1000	Decomposition	H_2, gas, carbon black

However, thermal cracking is indispensible as it is a source of primary petrochemical products, i.e ethylene, which is produced by thermal cracking of straight run naphtha and gas-oils and this process, is called steam cracking.

- ***Visbreaking***

Visbreaking is a mild thermal cracking process utilized in the refinery to reduce the viscosity and/or improve the pour point of a heavy oil, mainly residues, **AR** and **VR** both. A typical visbreaker unit is shown in **Fig.15**. In this process, the residual oil is heated at a desired temperature in a furnace and then rapidly transferred to a soaking drum, where, cracking occurs for a desired residence time up to the desired degree of cracking.

The cracked products are quenched immediately by exchanging heat with gasoil or cold visbroken tar to stop the cracking reaction then and there and prevent coking thereby. This type of visbreaking is called a soaker type visbreaking. In this type, the cracking reactions are initiated in the furnace but the progress of the reactions take place in the soaker drum. Another type of visbreaking operation is coil type, where, the cracking reactions occur in the furnace coil. Here the residence time of the reactions are kept as short as possible to avoid much coking. A long coil is normally used to complete the desired degree of reaction. The cracking temperature used in soaker type is normally lesser than that of coil type and hence, the coke deposition is also less in case of the former one.

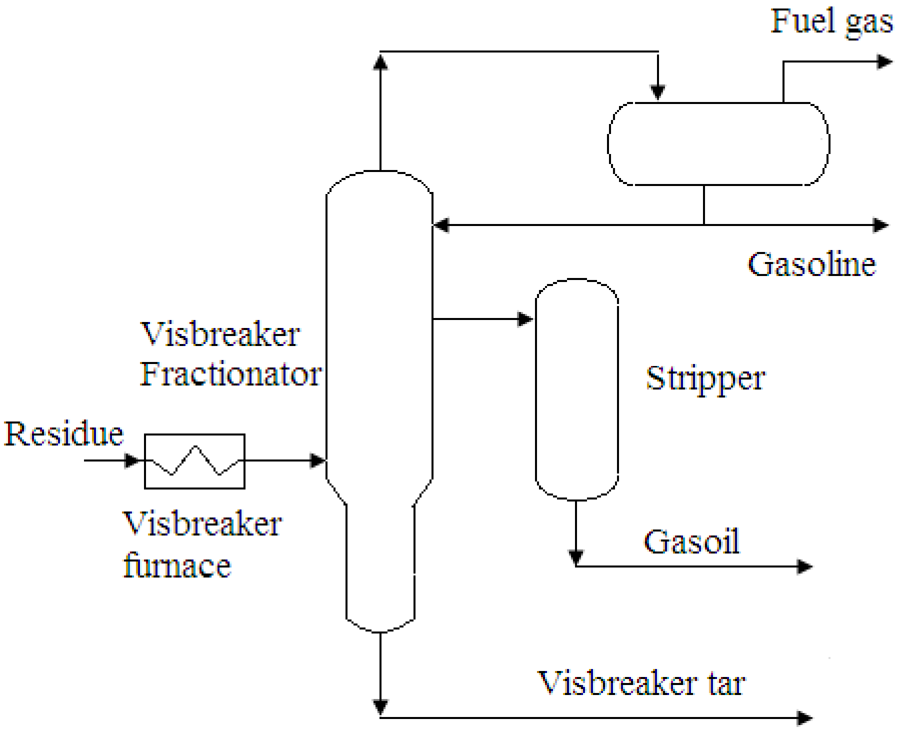


Fig.15. Visbreaker unit

The products obtained from visbreaking are gas, middle distillates and stable fuel oil. Visbreaking is often used to increase the middle distillate yield in the refinery by reducing the amount of heavy oil or bottom of the barrel (residual oil). This distillate fraction is used as a blending agent of fuel oil to reduce its viscosity. This distillate replaces diesel in refinery which is actually used as the blending agent. Hence, economics is strongly driven by the benefit of distillate production and the cost of visbreaking.

- ***Hydrocracking***

Hydrocracking is an operation in which low-value gas oil with a high percentage of polynuclear aromatics is simultaneously cracked and hydrogenated to produce low-boiling and mid-boiling distillates which are of high value. The primary advantage of hydrocracking is that, it selectively produces gasoline, diesel fuel or jet fuel by cracking and hydrogenation of polyaromatics, without producing any unwanted low molecular weight gases. The first modern hydrocracking unit was developed by CheVRon in 1959 which is known as CheVRon Isocracking Process. Hydrocracking is widely accepted by the refiners because of its ability to produce high quality products. Except gasoline and middle distillate this process gives lube oil base stocks and heavy oil suitable as the feedstock for catalytic cracking. A flow diagram of hydrocracking unit is shown in **Fig.16** below. Light coker gas oils and light cycle oils were used as feedstocks for hydrocracking earlier, but as the technology is improved, industry can take up heavier straight run vacuum gas oil, coker gas oil and solvent deasphalted oils as the feed for the process.

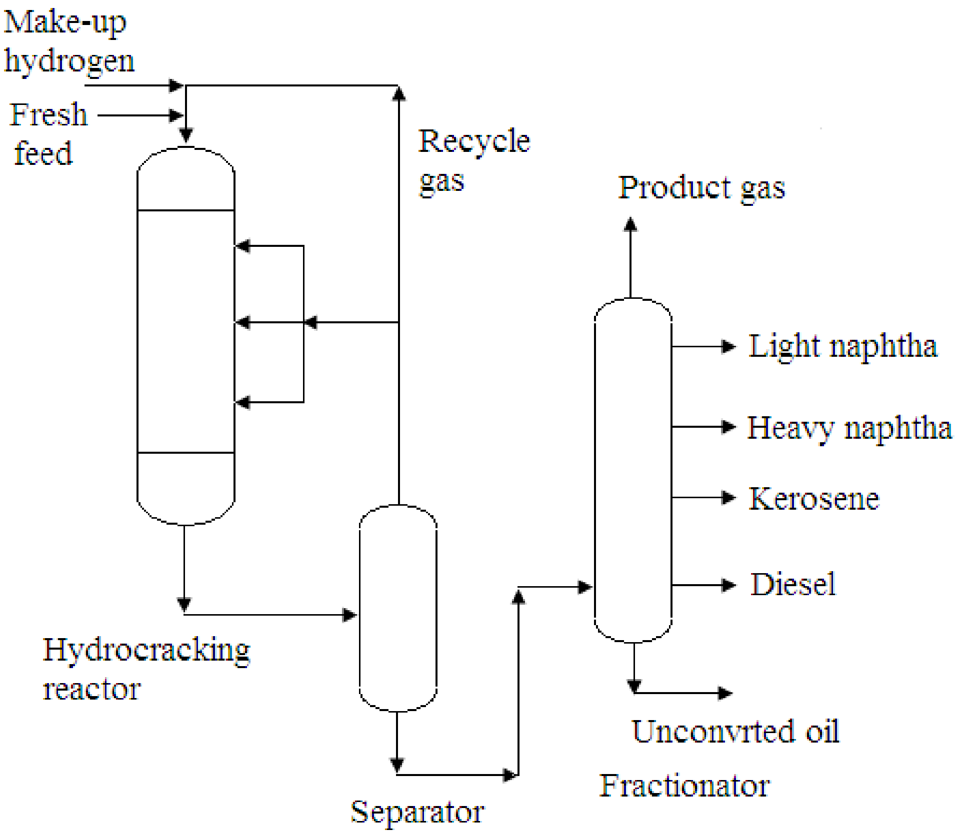


Fig.16. Flow diagram of hydrocracking unit

Hydrocarcking feedstocks are complex mixtures of mainly paraffins, naphthenes and aromatics. The boiling range is **345^0C+**. As the feedstock is passed through the reactor, aromatics are the first components to react; mainly forming naphthenes, which boil in the same range of **345^0C+**. Hence the amount of naphthenes of the same range increases. After most of the aromatics are converted to naphthenes, the naphthenes start to crack and the boiling point drops below **345^0C**.

Paraffins do not show significant cracking reaction in this single pass operation. Hydrocracking reactions are inhibited by the presence of nitrogen and sulphur compounds. Those compounds are mostly removed by this process when nitrogen compounds are converted to ammonia and sulphur compounds are converted to hydrogen sulfide. Conversion of sulphur compounds is easier than the nitrogen ones, as the former requires lesser hydrogen partial pressure. A precaution should be made in recycled hydrogen gas which should be free from any contamination of ammonia.

Hydrocracking can be done either thermally or catalytically, but the most common hydrocracking is catalytic. Hydrocracking catalysts mainly consist of active metals on solid acid supports where the acidic part of the catalyst serves the cracking function and the hydrogenation function is provided by the metals. The acidic supports are mainly amorphous silica-alumina, crystalline zeolite or a mixture of two. The metals that are used for performing hydrogenation are palladium, platinum, molybdenum, tungsten, cobalt or nickel.

❖ Coking

Coking is a refinery operation that upgrades low-valued bottoms like atmospheric or vacuum residue into higher-value petroleum coke. Petroleum coke is a high carbon coal like material. The process is actually a severe thermal cracking which completely converts the petroleum residues into coke and lighter products. The heavy distillate fraction which is produced in the process is recycled. The temperature used in this process ranges from **500 to 650^0C**. There are two basic forms of coking operation, Fluid coking and delayed coking. The first one is a continuous process and utilizes a fluid bed. The second process is a semi-continuous and uses coke drums for accumulation of coke. Delayed coking is more commonly used process in refinery. The name of the process ‘Delayed’ is due to the reason that, coking reaction occurs in the coke drum rather than in the heater. Coke drums are used to hold or delay the heated feedstock while the cracking takes place. The cracking/carbonization reactions involve dehydrogenation, rearrangement and polymerization.

- **Fluid coking**

Fluid coking is a continuous process in which heated feedstocks are sprayed into a fluidized bed of hot coke particles. The reactor is maintained at **20-40** psi and more than **500°C**. The feed vapors are cracked on the fine coke particles while forming a liquid film on the coke particles. The particles grow by layers until they are removed and new seed coke particles are added. The main unit of fluid coking process is the combined scrubber-reactor assembly, where the scrubber is fixed above the coker reactor as shown in the **Fig.17**. The residue feed is introduced into the scrubber at about **570^{0}C**. It is heated with the effluent stream of the reactor.

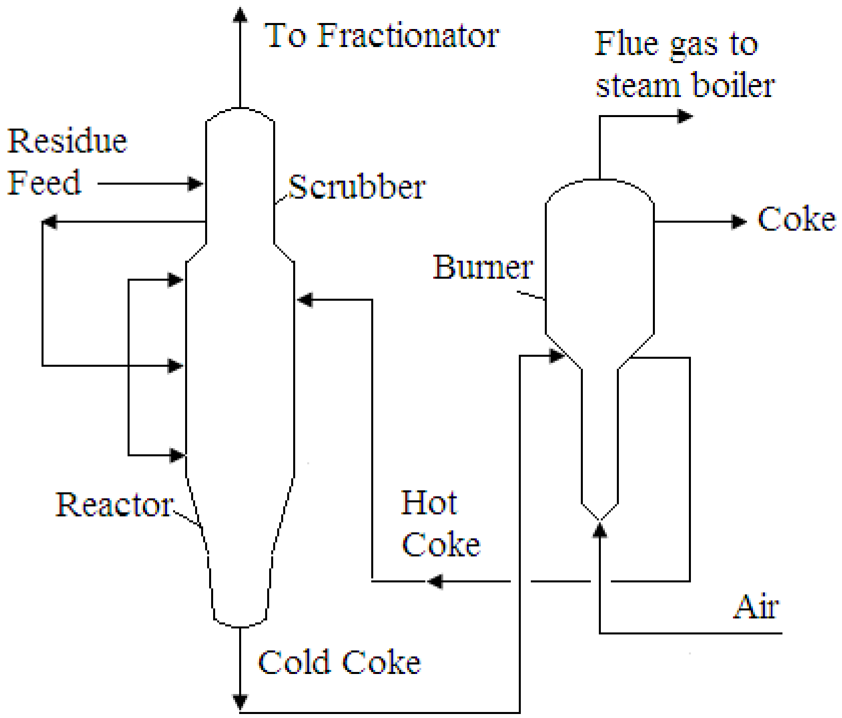


Fig.17. Fluid coking unit

In this scrubber, the high boiling hydrocarbons are condensed and scrubbed out with the reactor effluent vapors at about **525^{0}C**. This stream is recycled to the reactor mixing with the fresh feed. The lighter hydrocarbons from the overhead of scrubber are sent to the fractionators for recovery of lighter products. In the reactor, the cracking reactions take place to finally produce the coke and lighter products. Coke is sent to the burner and about 20% coke is burnt here with air to satisfy the heat requirements of the reactor in the cracking reactions. A part of the coke from the burner is recycled to the reactor and the rest is taken as a marketable product coke. The flue gas from the burner is used for steam generation in CO boiler.

- **Delayed coking**

Delayed coking is the preferred choice of many refiners as it imparts the advantage of handling very heavy residue. This process produces a significant amount of naphtha and diesel products. Moreover, the yields of product can be tailored by adjusting the recycle and operating conditions.

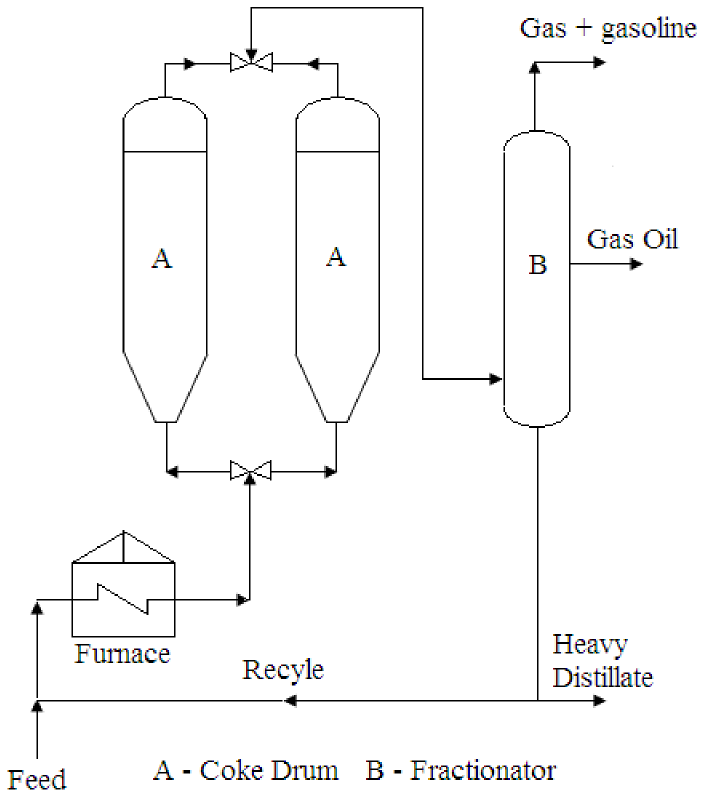


Fig.18. Delayed coker unit

Delayed coking is a semi batch process which uses alternative coke drums one of which is switched off-line after filling. Except coke drum, a furnace, closed blow down, coke cutting and handling and a water recovery system are included in the unit. Hot residual oil is mixed to the bottom of the fractionators (heavy distillate from fractionators) and the combined stream is heated in the furnace to initiate coke formation in the coke drums. Steam is injected in the furnace coil to avoid coking in the coil. Coke drum overhead vapour flows to the fractionator where it is separated into wet gas, unsterilized naphtha, gas oil, heavy gas oil and recycle. The Delayed coking unit is shown in **Fig.18** above. In the operating coke drum, the hot feed from the coker furnace is injected into the bottom of the drum at high temperature and low pressure and is cracked into gaseous products and coke. The gaseous products are sent to the fractionator for product recovery and the solid coke is solidified in the coke drum. The other drum which is offline and full of coke, is steamed, vented, and cooled prior to the drum being opened to atmosphere. During the coke drum steam out and cooling period, all steam and hydrocarbon vapours are directed to the blow down system where they are recovered. After this drum is opened, the petroleum coke is cut from the drum using high pressure water jet. The coke is dropped into a pit from the drum where water is separated from coke and recycled. Petroleum coke or simply “coke” is similar to coal and is typically used for fuel in power plants. There are two distinctive types of raw petroleum coke, one is calcined or green coke and another one is fuel grade or Petcoke. Fuel-grade coke is spongy in texture and contains high amounts of sulfur. It can withstand high heat and contains little ash. This type of coke is primarily used as a fuel in power generators. As it contains high sulfur, hence, burning of it produces sulphur dioxide gas. So, a sulfur capture system should be there to reduce the amount of sulfur released into the air and meet clean-air standards. Calcined petroleum coke is made by calcining or roasting petroleum coke just below the melting point. This coke is commonly used as electrodes in the smelting industry for the production of metals such as titanium, aluminum and steel.

Although, coke is a low value by-product compared to transportation fuel, there is a great demand worldwide for even high sulphur petroleum coke as it is a very economical fuel. Calcination grade raw petroleum coke (RPC) is produced at Barauni, BRPL, Digboi and Guwahati refineries of Indian Oil Corporation (IOC). Fuel Grade Petcoke is product at Panipat refinery of IOC.

❖ Catalytic cracking

- **Introduction**

Catalytic cracking is the process where low-valued high boiling feedstocks are cracked into value-added products by using a catalyst. Previously there were two types of catalytic cracking practiced in the refinery, moving bed catalytic cracking and fluid bed catalytic cracking. But eventually, fluid bed catalytic cracking proved to be advantageous and superior over moving bed and hence the later one is no longer used in the refinery. **Fluid Catalytic Cracking (FCC)** and **Resid Fluid Catalytic Cracking (RFCC)** are the two important cracking operations used in the petroleum industry where high boiling gas oils (>**350^0C**) and residues are converted into high octane gasoline, light distillate oil and liquefied petroleum gas. **FCC** is a continuous process where atomized feedstock is brought in contact with fluidized catalyst in a reactor. The heavy feedstock is cracked to lighter products at temperature above **500^{0}C** and the catalyst is deactivated. The products are separated from the catalyst and then the catalyst is sent to a regenerator. In regenerator, the residual carbon on the surface of the catalyst powder is oxidized at a high temperature (over **600^{0}C**) and regenerated. Regenerated catalyst is recycled to the reactor.

In the early 1960's, M.G.Kellogg and Phillips Petroleum began the development of residual oil cracking. It was clear that high carbon residue of these feedstocks would result in high coke yield compared to gas oil unit at the same conversion. Moreover, these were contaminated with high metal content such as nickel and vanadium, which resulted in deposition of metal on catalyst which in turn increased the yield of light gases, especially hydrogen. Residual oil cracking got significance when crude oil price was increased and availability of light crude was decreased, a demand for producing light transportation fuel was grown high, at the end of 1970's. In response to this pressure, two new residual oil cracking technologies- the '**UOP** residual oil cracking technology' and the 'Total catalytic cracking technology' were developed to compete with heavy oil cracking. Both of these technologies cope with the problem of excess coke production by using two stage regeneration. Depending on the level of contamination by metal and alphaltene, the residual oil feeds may be deasphalted or hydrotreated.

The common feedstocks of modern catalytic cracking are: gas oils from different origin (such as, atmospheric column, vacuum column, coker unit and thermal cracker), solvent deasphalted oil, lube-oil extract and bottom product of hydrocracker fractionators. **FCC** catalysts are mainly high silica to alumina Y-zeolites, ion exchanged by either rare-earth element or ammonium-ion. The catalyst is a fine solid having particle diameters in the range of 60-70 m and at this size, the catalyst particles are easily fluidized by hydrocarbon vapours in the riser reactor. The catalyst particles are of high attrition resistance to prevent the fracture due to high speed vapour and steam jets.

- **Process description**

There are four major sections in the **FCC** plant: converter, flue gas train, main fractionator and vapour recovery section. Converter can be subdivided into riser reactor, catalyst stripper and regenerator. **Fig. 19** shows the FCC converter. Cracking reaction occurs in the riser reactor. In this part, preheated feedstock along with recycled feed is atomized at the bottom of the reactor. When the atomized feed comes in contact with the hot catalyst powder, it vaporizes and cracks into smaller molecular weight compounds. The feed vapour carries the catalyst powder up to the riser as a dilute suspension. With the progress of the reaction, coke is continuously deposited on the catalyst powder and by this way, the catalyst loses it activity very soon. The feed atomizer is a conical shaped piece consisting of a number of flat fan-shaped spray nozzles. These spray nozzles atomize the feed in such a way that uniform coverage, to prevent bypassing of the catalyst powder, and maximum penetration of the feed into the catalyst particle occur.

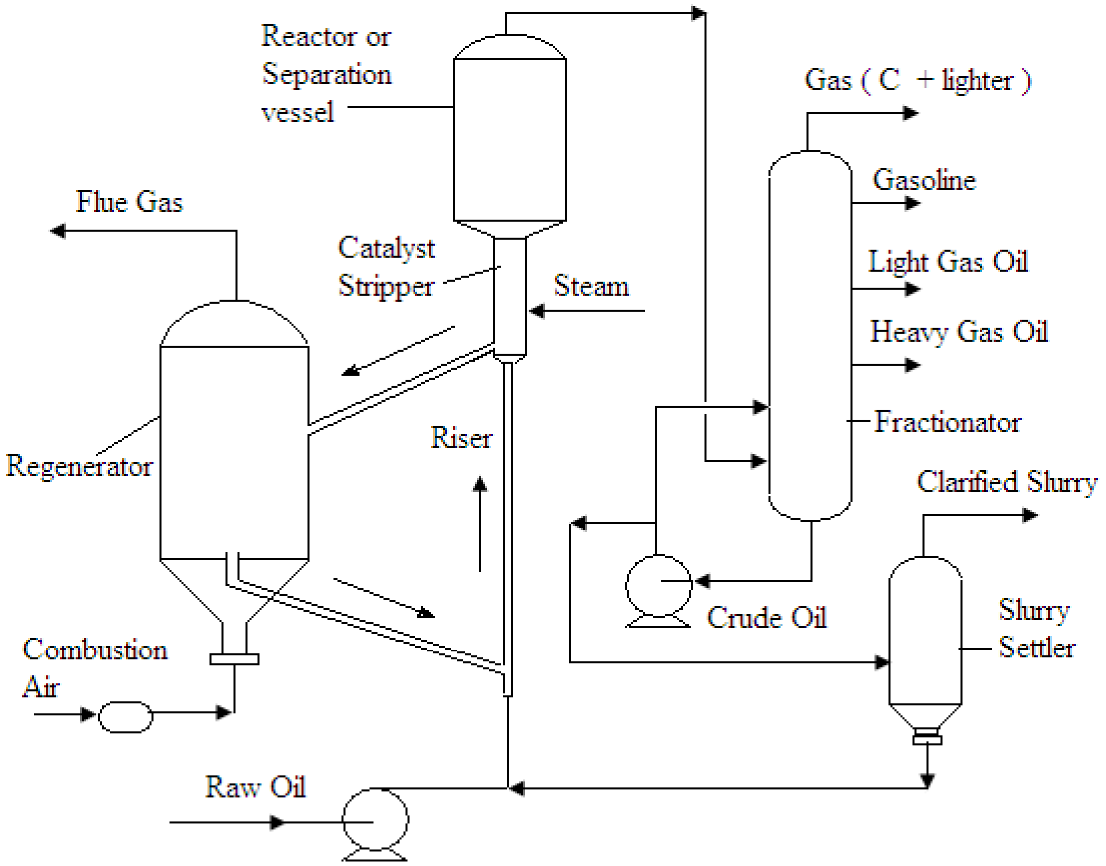


Fig.19. Fluidized catalytic cracking unit

The catalyst after getting deactivated by the coke deposition is separated from the reaction products by cyclone separators located in the disengager, at the end of the riser. The separation of catalyst particle and reaction mixture stops the cracking reaction automatically. Product vapours after separation flow through the disengager overhead line to the vapour recovery section. In this section, product vapours are quenched and sent to the main fractionator. The product vapours are not allowed to stay long in the disengager line, as at this place thermal cracking of the products may occur to produce low valued gases. The spent catalyst after getting separated from the products is sent to a two-stage steam stripper. Steam strips off the hydrocarbon contamination of the catalyst particles from the surface and within. This way, steam stripping minimizes the hydrocarbon carry over by the catalyst particles to the regenerator, which in turn imparts the advantages of lower regeneration temperature and lesser probability of catalyst deactivation due to sintering at high temperature. Hence, catalyst regeneration should be done at such an environment which can retain the catalyst activity and selectivity to a maximum possible extent.

After steam stripping, the coked catalyst particles are sent to regenerator where coke is removed by oxidation with air at high temperature. Air is supplied by high volume air blower which discharges air at low pressure. Air is passed counter-current to the catalyst. Spent catalyst is charged at the top of the regenerator and distributed uniformly. Air is introduced from the bottom. Combustion of coke produces mainly carbon dioxide, although some amount of carbon monoxide can also be expected due to incomplete combustion. The carbon monoxide content of flue gas is maintained below 200 ppm. The amount of coke deposition on the catalyst depends on the type of feedstock charged to **FCC**. The lighter feed produces lesser coke while heavy feed deposits higher amount of coke on catalyst. Moreover, the feed containing asphaltene and metals is responsible to produce more coke. Asphaltene is a precursor of coke production and metals catalyse dehydrogenation reaction of the feed compounds. Both of these aggravate the production of extra coke on the catalyst surface. This situation occurs in **RFCC** unit. After regeneration, the catalyst powders are cooled to the reactor temperature by the use of a catalyst cooler. High pressure steam is generated here. The heat from the flue gas obtained from the regenerator is recovered by a flue gas expander in the form of shaft work, i.e, mechanical energy and also by generating superheated steam. After heat removal, the flue gas is sent to a scrubbing unit and/or an electrostatic precipitator to remove **SOx** and particulate matter as per environmental laws.

The product vapours obtained from the disengager is condensed and the condensed liquid is separated into different cuts in the main fractionator. The products obtained from the fractionator are wet gas and unsterilized gasoline as the top product, light cycle oil as middle product and a heavy bottom product. The cycle oil is striped to remove light ends. Unsterilized gasoline is sent to a debutanizer to remove C4 cuts and thus the gasoline is stabilized.

The last unit of the whole operation is vapour recovery section, where **C2** to **C4** cuts are recovered from wet gas and gasoline. **C3** and **C4** cuts are utilized as LPG components. Sometimes a depropaniser is used to separate propane and propylene and a gasoline splitter is used to separate light and heavy gasoline according to the requirement.

❖ Reforming of naphtha

• Introduction

This refinery process is used to upgrade low octane naphtha to high octane motor fuel, which after reforming is termed as ‘reformate’. The hydrocarbons content of naptha are paraffins, naphthenes and aromatics in **C5** to **C12** range. This process involves the reconstruction of naphtha constituent of hydrocarbon molecules without changing the boiling range. Naphtha obtained from catalytic or thermal cracking operation contains some olefins also. The reformed naphtha or reformate is rich in aromatics and isoparaffins. Hydrogen is produced in this process which is used in hydro processing of different cuts in the refinery. Reforming is accomplished by processing the naphtha feed at elevated temperature (**450-520^{0}C**) and moderate pressure (**4-30 bar**) in presence of hydrogen. Catalyst used is mainly platinum based. The chloride treated alumina is used as support to improve acidic sites of the catalyst. The reforming unit practiced in the refinery are of two types, one is semi regenerative reforming, where the catalysts are regenerated in a cycle of 1 to 2 years and another type is continuous regeneration type, where each catalysts particles has a cycle time of typically 6 to 8 days between regenerations. **UOP (Universal Oil Product)** first commercialized the reforming process in the year 1949, who coined the process as ‘Platforming’, after the name of the platinum catalyst used by them. They also developed the continuous catalyst regeneration (CCR) system in the operation and this system along with catalyst modification can upgrade naphtha upto 108 octane number.

• Reaction chemistry of reforming

Four major reactions of paraffins and naphthenes occur in this process. These are,

1) Dehydrogenation of naphthenes

Dehydrogenation of naphthenes to the corresponding aromatics is a fast process. It is endothermic reaction and favoured by high temperature and low pressure. One example of this reaction is the conversion of a naphthene, methyl cyclohexane to toluene. This reaction releases three moles of hydrogen per mole of naphthene and upgradation of octane number of more than 25 units.

2) Isomerisation of naphthenes and paraffins

An example of isomerisation of naphthenes is conversion of alkyl cyclopentane to cyclohexane. Aromatization of cyclohexane is the next step which improves the octane number. Isomerisation of naphthene involves ring opening and ring rearrangement. Isomerisation of paraffins produce isoparaffins from normal paraffin, thereby increases octane number, for example, when n-hexane is isomerised to form 2-methyl pentane, then octane number increases from 25 to 74.

3) Dehydrocyclisation of paraffins

This reaction is a difficult reaction as it involves both cyclisation and dehydrogenation of paraffin. It is favoured by low pressure and high temperature. One example of this type of reaction is the conversion of n-heptane having zero octane number in the octane scale to methyl cyclohexane, having octane number 75.

4) Hydrocarcking of paraffins

Hydrocracking of paraffins is a reaction which occurs with the hydrogen liberated from other reactions of reforming. It is a high temperature and high pressure process. In this process some unwanted lighter products are obtained which boil below gasoline range. Hence, total liquid yield is diminished.

Types of reforming process

Semi-Regenerative Reforming (SRR) is the most common type of the catalytic reforming unit. This process is continuously carried out for a long period of time and catalyst activity gets reduced with time due to coke deposition. As the activity of the catalyst decreases, the aromatics conversion and the yield of hydrogen decreases. Hence to maintain almost constant yield, the reactor temperature is increased as catalyst activity declines. When the catalyst activity decreases to a very low level, which is called ‘end-of-cycle’, catalyst regeneration is started in situ by shutting down the reactor. Usually, **SRR** is operated at high pressure to maximize the time gap between two successive regenerations.

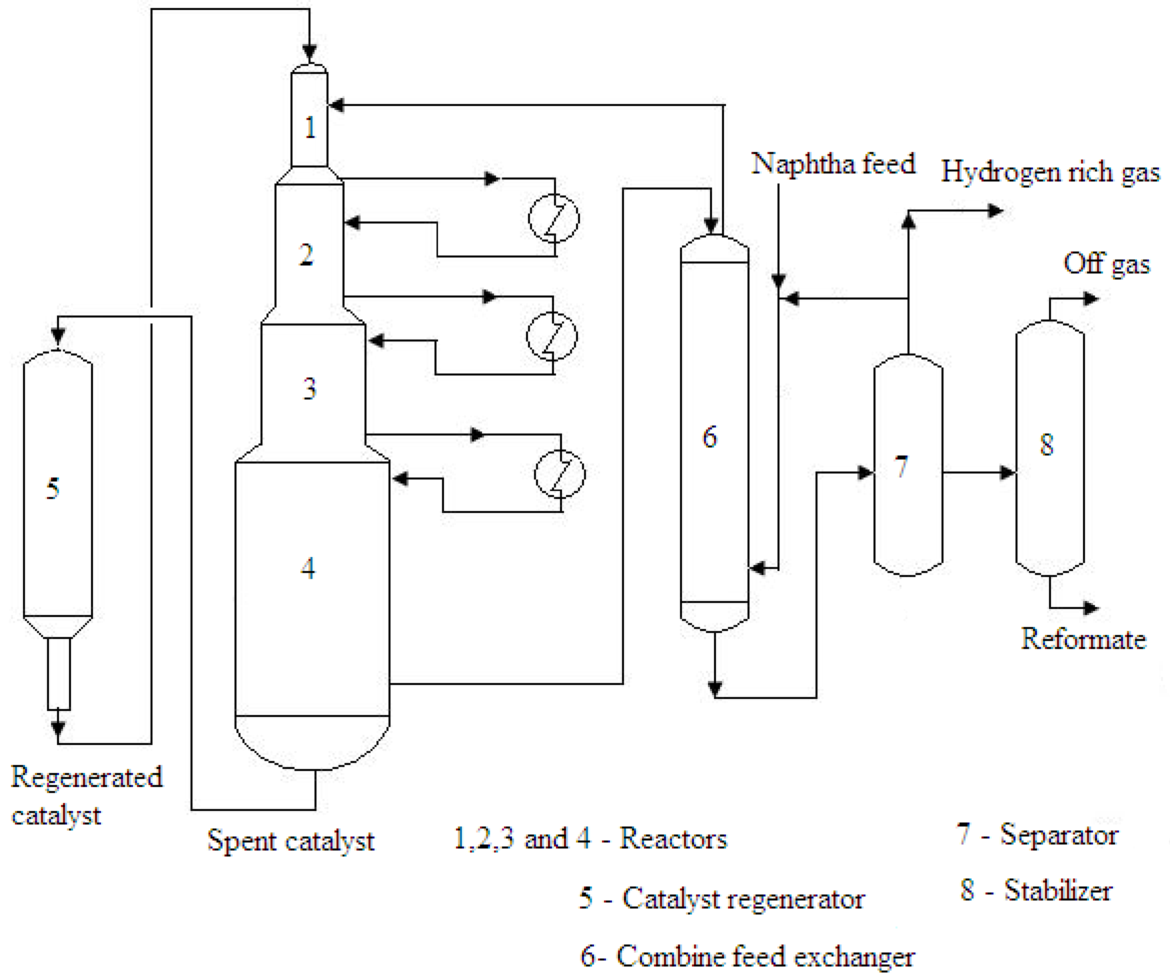


Fig.20. Continuous catalyst regeneration reforming unit

High reactor pressure minimizes coke formation on the catalyst. The time gap between two successive regeneration is usually 6–24 months. The **Pt–Re** catalyst is suitable catalyst for **SRR** units because it can tolerate high coke deposition and regenerates easily. The semi-regenerative system is generally designed keeping three to four catalyst reactors in series. **Continuous Catalytic Regenaration (CCR)** is the recently developed and most modern type of the catalytic reformers. A schematic of the process is shown in **Fig.20** In this process the regeneration of catalyst is done continuously in a special regenerator and then the regenerated catalysts are charged to the operating reactors. **CCR** process can handle low quality naphtha feed and produce high octane number. Hydrogen yield is also high in this process. Platinum/tin on alumina catalyst is mainly used in **CCR** process as the addition of tin enhances the selectivity to aromatics, improves stability, and regeneration ability of **Pt/Al_2O_3**. Reactors may be arranged either separately one after the other or stacked on top of one another and the catalyst moves from the bottom of one reactor to the top of the next reactor. The regenerated catalyst is charged to the first reactor and the deactivated catalyst is withdrawn from the last reactor and sent back to the regenerator. The difference between SRR and **CCR** process is that, selectivity towards aromatics is more important in **CCR** process than **SRR**, while tolerance of high coke deposition of the catalyst is one of the prime factor in SRR as the regeneration cycle time is much more here, than that of **CCR**.

- **Process description**

Naphtha feed after hydro treatment to lower the sulphur and nitrogen content, is mixed with the hydrogen formed in the process and introduced into a heater. Then the hot feed is charged to the first reactor at around **500^0C** temperature and 500 psig pressure. In this reactor, the fast endothermic naphthene dehydrogenation reaction takes place. Due to endothermic reaction the temperature of the feed falls down. The feed is then sent to the second reactor through a second heater. After other reactions take place at this stage, the feed is finally sent to the third reactor via third heater where final reactions occur. The hydrogen produced in the process is collected and recycled in the process. Reformate produced is heat exchanged and sent to a fractionator to remove light products to stabilize it. The high octane reformate is collected at the bottom of the fractionator at specified Reid vapour pressure. Catalyst deactivation is minimized by maintaining high hydrogen to hydrocarbon molar ratio (~6:1). The **CCR** process has the advantage of regenerating the catalyst continuously hence the catalysts are essentially contributing its original activity all the time in the reactor. So, the unit can operate at lower pressure upto 50 psig regardless of coke deposition on the catalyst.

- **Hydrotreatment**

Hydrotreatment is the refinery process which involves catalytic conversion and removal of sulphur, nitrogen, oxygen and metals from petroleum crudes and petroleum fractions at high hydrogen pressures. Hydrotreatment also includes hydrogenation of unsaturates and hydrocracking of higher molecular weight compound of petroleum fraction to lower molecular weight molecules. The increased application of hydrotreating can be ascribed to ***1) decreasing availability of light, sweet crudes and thus increasing fraction of heavy sour crudes that must be processed, 2) upgrade the feedstocks for catalytic reforming and catalytic cracking, 3) follow strictly the environmental regulations on sulphur limits in the fuels.*** The sulphur removal process in refinery is one of the most important units, called **hydrodesulphurization (HDS)**. This process is used to meet sulphur specification of fuels. Sulphides, disulphides, mercaptans, thiophene and its aromatic derivatives are the major undesirable sulfur compounds present in the petroleum fractions. Sulfur reduction in petroleum fuels is gaining importance due to the increasing consciousness about the serious consequences of burning sulfur-bearing fuels. The U.S. ***Environmental Protection Agency*** (**EPA**) had constituted new sulfur standards of diesel fuel and gasoline to 30 ppm by 2004 and 15 ppm by 2006, respectively. The Indian government has issued a notification to introduce Euro IV standards and 50 ppm sulfur fuel in 11 metro cities in April, 2010. In refinery, **HDS** is done mainly to gasoline and gas-oil cuts, to meet sulphur specification. In **HDS** process, feed and hydrogen gas are mixed together and heated to the reaction temperature in a furnace and also in a heat exchanger. It is then fed to the reactor where catalyst converts sulphur compounds to $\mathbf{H_2S}$, saturates olefins and some aromatics, at the reaction condition. The aromatics saturation is needed for meeting smoke point specification for kerosene. The catalyst used is cobalt-molybdenum on alumina, if the main aim is to remove sulphur and saturate olefins, but nickel-molybdenum on alumina is used when the aim is mainly aromatics saturation. Hydrogen partial pressure is an important parameter which ranges from 20 to 40 bars, depending on the type of feedstock. Hydrogenation reactions are exothermic and the catalyst bed temperature is maintained by external cooling and addition of recycle hydrogen. The operating temperature varies from $\mathbf{340^0C}$ at the start of the run to $\mathbf{370^0C}$ at the end of the run. The residence time of the feed in the reactor increases with increase in sulphur content. If residence time is kept constant then with increase in sulphur content, either the catalyst volume or hydrogen partial pressure should be increased.

- **Dewaxing**

The lube bearing crude contains an appreciable amount of paraffin wax in the lube oil boiling range. Much of these waxes should be removed from lube oil fraction to attain desired pour point specification. Two types dewaxing processes are mainly used in refinery:

1. Solvent dewaxing

2. Catalytic hydrodewaxing

Solvent dewaxing is done by utilizing a proper solvent which can successfully remove wax from the lube oil cut. This process involves the steps: crystallization, filtration and solvent recovery. In the crystallization step, solvent is added with the feedstock and the diluted feed is chilled at a temperature where wax components are solidified. The solid wax is filtered to remove it from oil. The solvent in the oil is recovered by solvent recovery step using flash distillation and stripping. The solvent is then recycled. The major solvent dewaxing process used in the refinery is **ketone dewaxing process**. Other processes are **Di/Me process** and **propane dewaxing process**. **Texaco process** and **Exxon Dilchill process** are the two major ketone dewaxing process. Texaco process uses a mixture of **methyl ethyl ketone (MEK)** and toluene as solvent. Suitable solvents in Exxon process include mixtures of **MEK** and **methyl isobutyl ketone (MIBK)**, **MEK** and toluene, dichloromethane and dichloroethane, propylene and acetone. Preferred solvents are ketones. Particularly preferred solvents include mixtures of **MEK** and **MIBK** and **MEK** and toluene. Both these ketone processes involve diluting the waxy feed with solvent and chilling the whole mixture at a controlled rate to produce slurry. Rotary vacuum filters are used to filter the slurry and the wax cake produced this way is washed with cold solvent to reduce its oil content. The cold filtrate is utilized to chill the feed stock and solvent mixture. Solvent is recovered from diluted oil and wax cake by flash vaporization and recycled to the process. The dewaxing solvent used in Di/Me process is a mixture of dichloroethane and methylene dichloride. Propane dewaxing process is almost similar to ketone process with the difference that, propane is used as the solvent. In this process, high pressure equipment is required and chilling is to be done in evaporative chiller by vaporizing a portion of propane. Propane dewaxing produces a better product than ketone process and does not require any crystallizer, but higher energy requirement is the main demerit of the former one.

Catalytic dewaxing process is less costly than solvent dewaxing process. Catalytic dewaxing or in other words, selective hydrocracking process has been developed to produce low pour point lubricating oil base stock. This process is based on reactions of selective hydrocracking of n-paraffinic hydrocarbons with formation of oils with improved low-temperature properties, fuel cuts, and gaseous hydrocarbons (propane-butane). The main outline of the process is hydrocracking in a reactor containing proprietary catalyst followed by a second reactor containing a hydro finishing catalyst to saturate the olefins formed in the first reactor. The base oils obtained by catalytic dewaxing are having improved viscosity at low temperatures. This is because of the unique properties of the catalyst used in this process, as it selectively separates linear paraffins from branched paraffins and does not remove all paraffinic hydrocarbons with a high melting point. This is the reason of low pour point but a good viscosity property of the base stock.

- **Deasphalting**

Asphaltenes are the high molecular weight compounds comprising of carbon, hydrogen, nitrogen, oxygen and sulphur with trace amounts of nickel and vanadium. These are high carbon: hydrogen ratio molecules, mostly condensed ring hydrocarbons and hetero-atom compounds. The hydrocarbons are precursor of coke formation in some refinery processes, heteroatom compounds are responsible for poisoning certain catalysts of the secondary processing and metals are particularly detrimental to cracking catalysts. Asphaltenes are removed by solvent extraction process. Solvent deasphalting is essential in production of high-quality conversion unit (**FCC and hydrocracking**) feedstocks. Typically light paraffinic solvents, such as, propane, isobutene, butane and pentane are used in the solvent deasphalting process. Olefinic solvents may also be used. The removal of asphaltene from oil depends upon the difference in solubility of **deasphalted oil (DAO)** and asphaltene in a particular solvent. Except this, solvent composition, temperature of operation and solvent to oil ratio are important parameters for separation. Typical uses of **DAO** are **lube oil base stock**, **hydrocracker feed**, **FCC feed** etc.

The feed for deasphalting is either atmospheric residue or vacuum residue. The feed is mixed with the solvent in the feed-solvent mixer and then this mixture is fed into the top distributor of the alphaltene separator. More solvent is counter currently introduced into the separator through the bottom distributor for efficient separation. Solvent does not dissolve asphaltene, but dissolve the oil into it. Hence, asphaltene is dropped out of the solution and comes through the bottom of the separator. The **DAO**/solvent mixture comes out from the top. **DAO** yield and quality are primarily dependent on the operating temperature. Higher temperature produces lesser quantity of **DAO**, where, lower temperature yields more **DAO** but quality drops down. The solvent cooler controls the operating temperature of the separator, and in turn controls the yield and quality of **DAO**. **DAO**/solvent solution, rich in solvent, is fed to a **DAO** separator to separate the solvent from DAO by heating above the critical temperature of the pure solvent. This is a supercritical phase separation step. After separation, the **DAO** containing some amount of solvent (in one volume of **DAO**, slightly less than one volume of solvent) is sent to a **DAO** stripper to separate the remaining solvent. Asphaltene obtained from the asphaltene separator is also associated with some solvent and is again introduced into an asphaltene stripper to recover the trace solvent. Superheated steam is used to strip off the solvent from both the components. The striped solvent vapour along with steam is obtained from the top of the stripper and then condensed. Water and solvent are separated and solvent is recycled to the process.

❖ Refinery equipments

- **Introduction**

In refinery, there are different types of equipments used for different purposes. It is difficult to include the description of all the equipments. Here, some of the important equipments are briefly discussed.

- **Pipe still heater**

Crude oils are heated in pipe still heater before entering into the atmospheric distillation column. This heater is a special type of furnace which heats crude oil upto about **350^0C** depending on the type of feed. A large number of tubes connected through bends are housed within the furnace in multiple rows. The still is built with two distinct heating sections, a radiant section, which can receive heat directly from the flame and a convection section, which takes heat from the hot gases travelling to the stack.

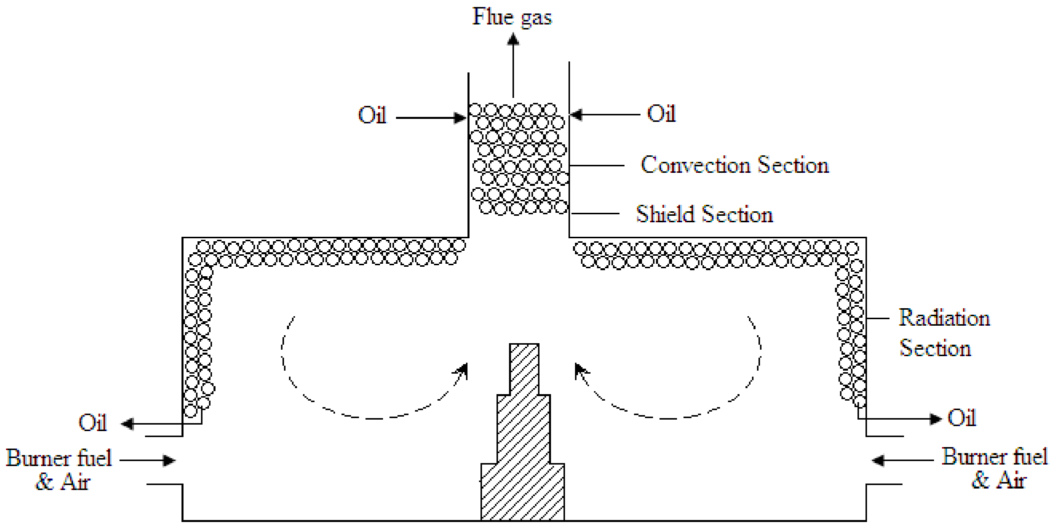


Fig.21. Pipe still heater

The hot flue gases arising in the radiation section flow into the convection section where they circulate at high speed through a tube bundle before leaving the furnace through the stack. Shield or shock section separates the two major heating sections. The tubes in this section are close to the radiation section that protects the convection section tubes from direct radiation. The shield section normally consists of two to three rows of bare tubes that are directly exposed to the hot gases and radiation flame. **Fig.21** depicts a pipe still heater. There are two major types of fired heaters, such as vertical cylindrical or box-type heaters depending on the geometrical configuration of the radiant section. In box-type heaters, the radiation section usually is of a square or a rectangular cross section. The tubes in the radiation section may be arranged horizontally or vertically along the heater walls and the burners are located on the floor or on the lower part of the longest side wall where there are no tubes. Box-type furnaces are mainly used where large capacities and large heat duties are required. In the cylindrical-type furnace, the radiation section is of the shape of a cylinder having a vertical axis and the burners are situated on the floor at the base of the cylinder. The vertical walls of the furnace are the heat transfer area and therefore exhibit circular symmetry with respect to the tube bundles. In the radiation section, the tubes may be arranged in a circular pattern around the walls of the furnace or they may have a cross or octagonal design which will expose them to firing from both sides. Crude oil is pumped into the furnace through the tubes at the convection section. At this section the crude is preheated and then goes to the radiation section to be heated upto **350^0C**. Heat transfer at a high rate is obtained by passing the crude with a high flow rate. The fired heaters have corrosion and material problems due to the elevated temperatures experienced both on the process side and in the fire-box. The Atmospheric Heater receives flashed crude at about **260°C** and sends it to the atmospheric column at about 350°C. For sweet crude, the radiant tubes and lower rows of convection tubes are typically 5% chrome with carbon steel in the up section.

- **Heat exchangers**

Different types of heat exchangers are used in refinery. If the hot stream is a vapour and is cooled without much condensation, the heat exchanger is called a vapour heat exchanger. If the vapour is condensed in the exchanger, then it is called a vapour denser exchanger. The vapour condensed in this way is then subsequently cooled in a exchanger which is called cooler or after-cooler. The heating equipment used to heat the bottoms of a fractionator is called a reboiler. Double pipe heat exchangers are common in refinery. Fins, either in spiral form or as longitudinal plates on the inside pipe in the double pipe Viscous or low-heat transfer rate fluids can be passed through the finned tube to get higher heat transfer area. Jet type condenser has application in refinery. Barometric jet type condenser is used in vacuum distillation to condense steam as well as create some vacuum. The working principle of this type of condenser is to mix the vapour and the cooling medium intimately by high pressure jets and heat exchange is done by mixing of the two streams or conduction heat transfer. In heat exchangers, the decision of which material (fluid/slurry) is to be passed through tube is dependent on different factors. Usually dirty streams are passed through tubes as the tubes in tube bundles can be cleaned, but sometimes, if the stream contains lots of coke or debris, then that should be passed through shell and shell may be disposed after certain time. High pressure fluids are passed through tubes as they can withstand high pressure but shell does cheap and the cleaning of deposition or water scale is easier in tubes than shell. Normally large volume liquids are passed through shell. The metallurgy of heat exchanger varies with temperature and the composition of stream. The material of construction for majority of the exchangers is 100% carbon steel. Admiralty brass tubes have been used in fresh water cooled exchangers to prevent water-side fouling and corrosion. Due to the high cost of the brass bundles and improvements in cooling water treatment, many brass tube bundles are replaced with carbon steel. In hot hydrocarbon service, 5% chrome materials in heat exchangers are mostly used. As the sulphur content in the crude increases, the use of high chrome tubes and 12% chrome shell and channel linings are required.

- **Fractionating tower**

Fractionating towers are the equipments which separate the components from a mixture. Crude oil atmospheric distillation tower is the most important fractionating unit in refinery. Distillation tower with bubble-cap trays is the most conventional and familiar design. The other types of trays used are sieve tray, perforated tray etc. Small bubble caps are best for large liquid loads and large caps are for large vapour load. Some designers use small cap for small tower and large cap for towers of 10 to 20 ft in diameter. Cast ion is largely used for bubble cap as it is more corrosion resistant than steel. In vacuum towers, pressed alloy steel caps are becoming important. Many caps are of removable types, i.e, the vapour uptake and cap are properly assembled on the plate, but sometimes this arrangement is not satisfactory as bolts rusts and cast iron caps may break. The atmospheric column is commonly lined more extensively than the preflash column because the feed, which is at about **350^0C**, is not only hotter but also contains larger amounts of HCl and H_2S. The top of the column is often lined with Monel 400 (about 67% Ni – 23% Cu) to protect against condensing HCl. Normally, the lower 2/3 or ¾ of the column will be lined with 12% chrome cladding to protect against high temperature sulfur corrosion. In the area of the feed inlet, or flash zone, 316 stainless steel may be required in those plants processing crudes high in naphthenic acid content.

- **Pumps**

Different types of pumps are used in the refinery as per requirements. Asphalts or semi-solid materials are handled with reciprocating steam pumps. For handling large amounts of medium viscosity oil, centrifugal pumps may be used. Centrifugal pumps are largely used for pumping non-viscous fluids because of their high capacity low head characteristics. But more viscous materials are handled by rotary pumps.

Gaseous Fuel

❖ Introduction

Gaseous fuels are obtained either naturally or by the treatment of solid or liquid fuel. Among the naturally occurring gaseous fuels, natural gas and liquefied petroleum gas are most important. These gases have high calorific value. 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 dimensional group, called Wobbe number or Wobbe index which is $\frac{CV}{\sqrt{sp.gr}}$.

Flame speed of a gaseous fuel is also an important parameter to make a classification and it is represented by the propensity of the gas to react. Flame speed is represented by a factor called Weaver flame speed factor, which is expressed on an arbitrary scale, where hydrogen is assumed to have 100 Weaver flame speed. It is defined as the ratio of the laminar flame speed of the gas of interest with that of hydrogen. The lower is the number the lower the flame speed. Weaver speed factor is greatly influenced by the amount of hydrogen in the mixture.

Gaseous fuels have lower energy content than liquid fuels such as, petrol or diesel. However, they are potentially more deserved fuel as they produce very low greenhouse gas upon burning and hence air quality benefits are obtained compared to conventional and petrol and diesel products.

❖ Natural gas

Natural gas is usually a mixture of methane, ethane, propane, butane, pentane and sometimes a small amount of C5+ hydrocarbons. The major constituent is methane. Except these, hydrogen sulphide is sometimes obtained in natural gas, although it is not very common. The natural gas containing high amount of hydrogen sulphide is termed as sour gas and that contains low amount of hydrogen sulphide is termed as sweet gas. Common but trace constituent gases are carbon dioxide and nitrogen with average proportions in the range of **0.5 to 10%** and 0.5 to 5% respectively.

Broadly natural gas is classified in **three types**:

1) Non-associated gas, which is not in contact with oil in the reservoir.

2) Gas-cap associated gas, which is overlying the oil phase in the reservoir.

3) Associated gas which is dissolved in the oil at the reservoir condition (solution gas).

<u>Gas-oil ratio (GOR)</u> is the ratio of the volume of gas to the volume of oil at normal or standard conditions of temperature and pressure. It determines the amount of gas dissolved in oil in a reservoir. GOR 1 represents that, 1 m^3 of gas is recovered at the separator per m^3 of oil extracted at normal temperature and pressure. This ratio varies from a few fractions of a cubic meter to more than 150 cm^3 of associated gas per m3 of oil. In **Fig 22**, description of different types of reservoir is shown. **Example 1** represents a dry natural gas reserve, which may contain some carbon dioxide and nitrogen along with lower hydrocarbon gases mixed with the major component methane. Gas is located above the water phase accumulated at the bottom of the reservoir.

Example 2 shows a picture of condensate gas. The reservoir contains liquid hydrocarbons in large proportions which are dissolved in gas phase.

In example 3, the quantity of liquid hydrocarbons phase is quite high, so that, at the thermodynamic condition of the reservoir, the liquid and gaseous phases co-exist. In this condition, the gas phase contains dissolved hydrocarbons of liquid range and liquid oil contains dissolved gases. Although the liquid phase is of sufficient quantity, but the major phase is gas, hence, the former forms an ‘oil-ring’ between the gas phase and water.

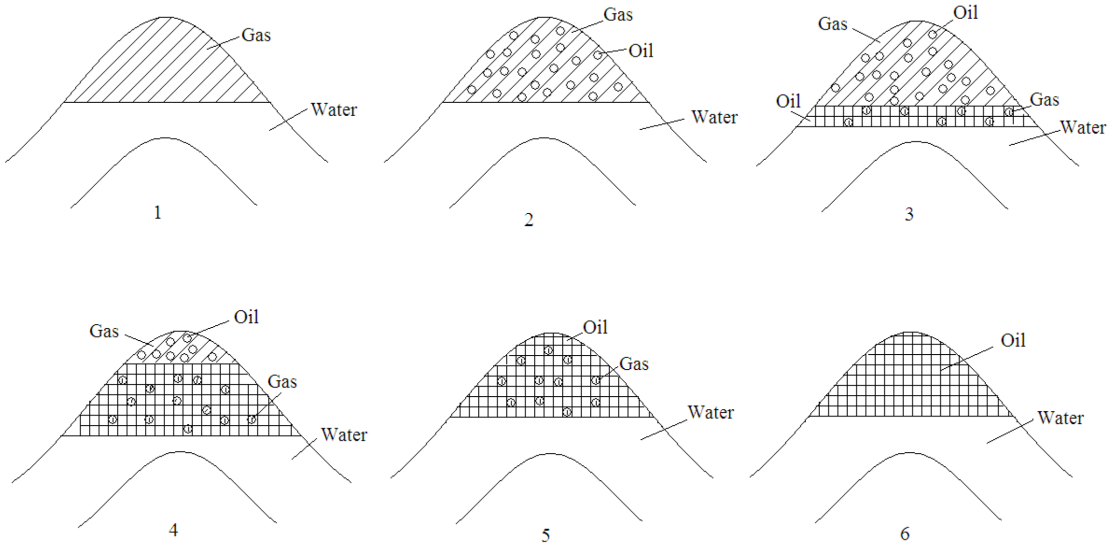


Fig.22. Gas-oil contact in different types of reserve

The reservoir shown in **example 4** has oil as its major component. This is primarily an oil reservoir containing a gas cap over it. The gases are dissolved in the oil and some oil is also dissolved in gas. **Example 5** shows an oil reserve having gas dissolved in liquid oil. The amount of gas is quite small in amount.

Example 6 depicts an oil reserve with no gas dissolved in oil.

Non-associated gas can also be 'wet gas', which means that it contains appreciable amount of ethane, propane, butane and some higher hydrocarbons. Except methane, other hydrocarbons are condensed to form 'condensate'. This condensate can be mixed with naphtha fraction. Natural gas has calorific value in the range of 8400 to 9100 Kcal/Nm^3. Hence, this is a high calorific value gas. **CNG** (**compressed natural gas**) and **LNG** (**liquefied natural gas**) are both the forms of natural gas or methane. Whilst it is common to confuse the two varieties, the key difference is that **CNG** is stored as a gas at a high pressure, whereas **LNG** is cooled to **-160^{0}C** which causes it to become liquid. Both the fuels are used in light passenger vehicles.

Natural gas hydrate is a cage-like structure of natural gas and water frozen together into a solid substance, which is mainly found in arctic permafrost regions and in sediments in the ocean's bed. Research is now going on to better understand this large fuel resource, how natural gas hydrates form, where they are located and how they could be used as a future source of natural gas. The potential of this vast resource may be more than the total reserve of oil, natural gas and coal all around the world. Several possible methods are investigated to recover the natural gas from its hydrates as this large amount of natural gas deposit may fulfill world's growing energy needs. Hydrates may also provide a novel way to store natural gas for transportation. Currently, natural gas travels primarily by pipeline. Solidified gas hydrates could be transported by specially designed ships, for example.

❖ Liquefied Petroleum Gas

Liquefied petroleum gas or **LPG** in short, is a colourless and volatile hydrocarbon gas which is obtained from refinery gas or natural gas (including associated gas in oilfields) through pressurizing, cooling and liquefaction. The constituents of **LPG** from refinery gas are mainly propane, propylene, butane, butylene, with a small amount of pentane and pentylene, as well as a little amount of sulfide impurities. **LPG** from natural gas scarcely contains olefins. **LPG** has main use as industrial and domestic fuel as well as combustion engine fuel. **LPG** is a flammable gas and explodes when its concentration in the air reaches a certain value. **LPG** remains in gaseous state at atmospheric pressure and normal ambient temperatures, but it can be liquefied when moderate pressure is applied or when the temperature is sufficiently reduced, and this way it is stored in cylinders.

Compared with other fuels, **LPG** has the following particular advantages of less pollution, higher heat generation because of its very high calorific value, ease of transportation by roadways (tankers) and waterways (vessels). Storage of **LPG** is also very convenient. It can be stored in tanks and can be filled in cylinders for customer use. **LPG** can also be supplied through gas distribution station and pipelines. Moreover, it is free of smoke, dust and carbon residue. Due to the above advantages of **LPG**, it is widely used as industrial, commercial and domestic fuel. In addition to these, **LPG** is a useful raw material for chemical industry. Pyrolysis gas produced from the thermal cracking and catalytic cracking processes is a major source of **LPG**. The major components of pyrolysis gas are hydrogen, methane, ethane, ethylene, propane, propylene, butane, butylene, and **C5+**. These hydrocarbons may be separated by cold separation process and **LPG** may be prepared by liquefying **C4** and **C5** gases which can be stored in cylinders. On opening the valve of the **LPG** cylinders, the flammable gaseous hydrocarbons pass through the pipes into the burner. **LPG** forms blue flame on ignition, giving out a large amount of heat during the combustion (with heat generation value of 92,100 kJ/m^3-121,400 kJ/m^3). The constituents of **LPG** can be separated and used to produce synthetic plastic, synthetic rubber, synthetic fibre, pharmaceuticals, explosives, dyestuff, etc. Although **LPG** is a convenient fuel but it is dangerous too. If the pipeline leaks or the valve is not tightly closed, **LPG** spreads into the room. When its content reaches the explosion limit, **LPG** will explode if it comes in contact with any sparks. Because of this nature of this gas, **LPG** processing plants often mix a little amount of bad odourous mercaptan or thioether derivatives with **LPG** to detect its leakage. When **LPG** leaks, it can be smelled instantly and corresponding emergency measures can be taken.

❖ Producer gas

Producer gas is a low calorific value fuel gas comprising of mainly carbon monoxide and nitrogen. It is produced by passing air or a mixture of air and steam through a burning bed of solid fuel such as, coal, coke, wood or biomass. Hydrogen is also present in a significant amount in the producer gas if air-steam blast is used. The exact composition of producer gas depends on the type of fuel, composition of the blast and operating condition. Producer gas is formed in a gasifier, called gas producer.

The reactions involved in gas producer are as follows:

1) When only air is used as blast through the fuel bed (air-blast),

a) $C + O_2 + N_2 \rightarrow CO_2 + N_2$

b) $CO_2 + C \leftrightarrow 2CO$

Reaction (a) is highly exothermic and occurs at temperature above **500^0C**. Due to heat generation by this reaction, the fuel bed temperature increases. CO_2 formed in that reaction reacts with carbon of fuel to form CO. This reaction is named as Boudouard reaction and this reaction is important in the sense that the main component of producer gas, CO, is obtained in this reaction. This reaction is endothermic in nature and is favoured at temperatures above **500^0C**. As a whole the net process is exothermic.

The overall reaction is

c) $2C + O_2 + N_2 \leftrightarrow 2CO + N_2$

The favourable condition for reaction is high temperature, sufficient time of reaction and reactive fuel. If the fuel contains ash of low fusion point, such as below **1100^0C**, it melts and re-solidifies into the cooler part of the fuel bed. This is called clinker and it disturbs the uniform burning of fuel and thus the overall efficiency decreases. The coals having big lumps are also not suitable as a good fuel due to non-uniformity of the bed. The lumps must be broken into small pieces for getting higher efficiency. After producer gas is formed in the bed, an opposite reaction to the Boudouard reaction may occur, which is called Neumann reversal reaction, to form CO_2 and C.

d) $2CO \leftrightarrow CO_2 + C$

2) When steam is used in admixture of air (steam blast)

At this condition, the above reactions occur (reactions a, b, c, d) and along with those, some other reactions also occur. Carbon reacts with steam to form carbon monoxide and carbon dioxide by the following reactions,

e) $C + H_2O \leftrightarrow CO + H_2$

and **f)** $C + 2H_2O \leftrightarrow CO_2 + 2H_2$

Both the reactions (c) and (f) are endothermic. The reaction (e) is active at or above the temperature **1000^0C** but reaction (f) occurs at the temperature range of **500 to 600^0C**. The later reaction (f) is not desirable as it produces CO_2, which is not a component of producer gas, hence, always the fuel bed temperature is kept high to avoid this reaction. The excess steam may also react with CO to form CO_2 and H_2 in water gas shift reaction as shown below. This is also an undesired side reaction.

g) $\mathbf{CO + H_2O \leftrightarrow CO_2 + H_2}$

Methanation or methane formation is another side reaction observed.

h) $\mathbf{C + 2H_2 \leftrightarrow CH_4}$

The above reaction is not favoured at high temperature.

There are several advantages of using steam blast over air blast. In steam blast, hydrogen and methane are the two gaseous components formed which add more calorific value to producer gas. The endothermic reactions (e) and (f), which occur in steam blast do not allow the fuel bed temperature to shoot up very high, and this way they prevent clinkering of bed to a great extent. Clinkering reduces overall efficiency. The optimum temperature required for producer gas manufacture is within the range **1100 –1300^{0}C**. There is some restriction on the amount of steam also. The endothermic reactions, (e) and (f) occur at a faster rate using large amount of steam, which thereby reduces the fuel bed temperature below **1100^{0}C**. Lower temperature of fuel bed encourages the carbon dioxide formation by the reactions (a), (f). Steam blast is formed either by injecting steam to the air or passing air through water. The first process is more convenient to use. The temperature of the air is raised by blowing steam into it upto a desired temperature. This temperature is called 'blast saturation' temperature.

- **Gas producer**

In the gas producer, the fuel bed is set on a metallic grate. **Fig.23**. depicts a fuel bed in a gas producer with different reaction zones. The zones are ash zone, oxidation zone, primary reduction zone, secondary reduction zone and drying zone. Different reactions occur at different zones of the bed. In a countercurrent movement of air-steam blast and solid fuel, the blast gets preheated at the ash zone. In the oxidation zone, carbon dioxide is formed by the reaction of carbon and oxygen of air. In the primary reduction zone, several reactions occur which produce carbon monoxide, carbon dioxide and hydrogen (reactions b, e and f). At this stage carbon monoxide formation is quite high. After this, secondary reduction zone starts where steam reacts with carbon monoxide to produce carbon dioxide.

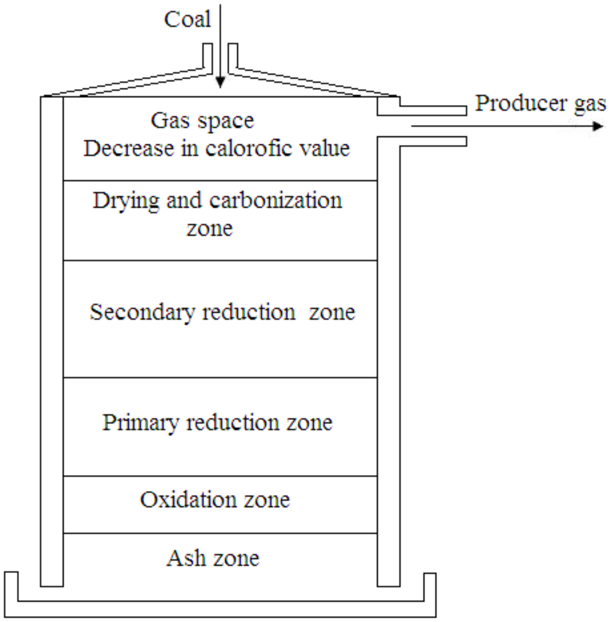


Fig.23. Different reaction zones in a gas producer

The topmost zone is drying zone where water vapour and volatile matter of the fuel are added to the gas. Hence, it is observed that, as the gas travels through the bed, its composition goes on changing at each point. The addition of volatile matter increases the calorific value of the exit gas. After the gas leaves the bed, it comes to the gas space above the bed. Here, water gas shift reaction (g) and Neumann reaction (d) occur, where, amount of carbon monoxide decreases. Hence, the composition of the producer gas is changed and a decrease in calorific value of the gas is observed.

Different types of gas producers are used in industry. Depending on the direction of fuel and blast movement, the producers are broadly classified as, up-draft, down-draft and cross draft producers. In these types of producers, the fuels move either countercurrent or concurrent to the flow of gasification medium (steam, air or oxygen) as the fuel is converted to fuel gas. They are relatively simple to operate in a fixed bed process. In an updraft fixed bed producer, the flows of the fuel and gases are countercurrent to each other. The reactive agent, i.e air-steam blast is injected at the bottom of the reactor and ascends to the top while the fuel is introduced at the top and descends to the bottom through zones of progressively increasing temperatures (drying, secondary reduction, primary reduction and oxidation). Heat from the primary reduction and oxidation zones rises upward to provide energy for the next zones. Gases, tar and other volatile compounds are distributed at the top of the reactor and increase the calorific value of producer gas, while ash is removed from the bottom.

In case of downdraft producers, the locations of the zones are reversed. The fuel is introduced at the top, and the reactive agent is introduced through a set of nozzles on the side of the reactor. Producer gas leaves from the bottom of the producer. Cross-draft producers exhibit many of the operating characteristics of downdraft gasifiers. Air or air/steam mixtures are introduced into the side of the gasifier near the bottom, while the producer gas is drawn off on the opposite side. Producer gas has a very low calorific value in the range of **1000 to 1200** Kcal/Nm^3. Applications include the use of it as fuel for industrial kilns and heat treatment furnaces, such as those found in steel plants. Producer gas is also usable in plants that melt zinc for use in galvanizing processes and for melting metals, such as aluminum and copper. It is used for heating open hearth furnaces in the manufacture of steel and glass. It is used for heating muffle furnaces and retorts in the manufacture of coke and coal gas.

Water gas

Water gas is a gaseous fuel generated in the similar way as producer gas, by gasifying incandescent bed of solid fuel with superheated steam. The gas is mainly composed of an equal proportion mixture of carbon monoxide and hydrogen. It is a low calorific value fuel; the calorific value is around 2800 kcal/Nm^3. The gas emits blue flame when ignited due to high content of **carbon monoxide**, hence, it is named as blue water gas.

The reactions involved when steam is passed through the burning bed of coal or coke above **1000^{0}C** are,

1) $H_2O + C \rightarrow CO + H_2$

This reaction is strongly exothermic and temperature falls below **1000^{0}C** gradually with the progress of the reaction. At lower temperature steam starts to react with carbon to form carbon dioxide, according to the following reaction,

2) $2H_2O + C \rightarrow 2H_2 + CO_2$

As carbon dioxide does not contribute to the calorific value of water gas, the above reaction is undesirable. To prevent the formation of carbon dioxide and to lower the cost of the process by not supplying heat from outside to the fuel bed, the whole process of water gas generation is divided into two stages,

a) Blasting period, when fuel bed is heated up by passing air through it by the exothermic reaction,

3) $C + O_2 \rightarrow CO_2$

Carbon dioxide formed in this reaction is converted into carbon monoxide by the reaction with the carbon of the solid fuel as the temperature of the fuel bed rises.

4) $CO_2 + C \leftrightarrow 2CO$

b) Run or gas-making period, when blue water gas is produced by passing steam through the incandescent bed of coal. At this period, along with the reactions 1) and 2), other reactions such as water gas shift reaction and methanation reaction also occur.

The objective of the blast period is to accomplish only reaction 1) to produce maximum possible heat by this exothermic reaction and the objective of run period is to produce carbon monoxide as much quantity as possible by utilizing maximum amount of steam. Both these objectives keeping in consideration, a fuel bed with moderate thickness is used, with enough contact time of steam with the bed. In practice, the rate of decomposition of steam and the formation of water gas are controlled by alternate blast and run period. As soon as temperature falls below **1000^0C**, steam blast i.e, run period is stopped and air blast period is started to raise the temperature of the fuel up to **1400^0C**. When this temperature is attained, the air blast is stopped and steam blast is again resumed. In this way, the process alternated. After the air blast period is over, the bed is purged with steam for 2 seconds to remove the carbon dioxide formed in the blast period and this way CO_2 is prevented to mix with the blue gas. This steam is called purge steam. On the other hand, after the run period, a 2 second air purging is done to remove last trace of water gas present in the generator, before the blast period is started. The period for which air is passed through the fuel bed is called hot blow. The run period is carried out for 3 min and this period is also called cold blow. The hot blow is done for about 1 min. In the modern period, it is aimed to decrease hot blow period and to increase the run period.

- **Gas generator**

The gas generator consists of a refractory brick lined steel cylinder with approximately 3 m dia and 5 m height. The solid fuel, coal or coke is introduced at the top of generator through an opening, provided with a door. Two inlet pipes with valves are fitted at the left side of the generator, where, one pipe is below the top and the other is above the bottom. Air blast is introduced through these pipes. Steam is passed through two sets of steam pipes, one set is located at the upper region and another set is at the lower region of the generator. The cyclic operation runs according to the following:

a) Up-stream period: At this period, steam is blown through the lower set of steam pipes and passed upward through the hot fuel bed to generate water gas. This period is carried out for 1.5 min. Water gas produced goes out from the generator by an outlet pipe located at the top.

b) Down-stream period: This period also takes 1.5 min. Steam is blown downward through the upper set of steam pipes to the fuel bed. The water gas produced leaves the generator through a pipe at the base. This pipe is connected to a vertical pipe which is again attached to the outlet pipe. So, water gas formed goes out of the generator through the outlet pipe.

c) The three minute run period (up-stream + down-stream) is followed by one minute purge with air to remove the remaining water gas and send that to the gas holders.

d) After the air purging, air blast is sent through the bed to increase its temperature up to **1400^0C**. This operation takes about 2 min. Carbon dioxide formed at this stage passed out through the top valve and thrown as waste.

- **Carbureted water gas**

Water gas is a low calorific value fuel gas. To increase its calorific value, water gas is carbureted by adding gaseous hydrocarbons obtained by cracking petroleum oils. In addition to the gas generator, a carburetor, a superheater with purifiers, scrubbers and condensers are used to produce carbureted water gas. Carburetor and superheaters are the two big steel vessels, lined with refractory checker bricks to provide intensive heat transfer surface. The gas produced at the air blast period contains large amount of heat which is passed through these vessels to heat the top and side walls and then escape through a chimney to waste heat boiler for raising steam. Water gas produced during the run period in the gas generator is passed to the carburetor at the top and hydrocarbon oil is sprayed through atomizer into the red hot fire brick. The sprayed oil in the carburetor is cracked. The products of cracking and the water gas pass down the carburetor and enter the superheater at its bottom. The gas mixture rises up through the superheater and the cracking process is completed at this stage. Some tar produced during cracking is separated in a separator. The gas then passed through a series of pipes cooled by water spray. After cooling, the gases are led to the purifiers and finally to the gas holders. In purifiers, hydrated ferric oxide and lime impregnated wood sharing are placed which remove hydrogen sulfide as iron sulfide. The calorific value of carbureted water gas is approximately **4500** kcal/Nm^3.

The composition of carbureted water gas is as follows:

H_2: 34-38%, CO: 23-28%, saturated hydrocarbons: 17-21%, unsaturated hydrocarbons: 13-16%, CO_2: 0.2-2.2% and N_2: 2.5-5%.

Water gas is used as a source of industrial hydrogen in the manufacture of methyl alcohol and carbureted water gas is used for welding purpose, and illuminating purposes.

Hydrogen gas is obtained in a very trace amount in atmosphere. It is found in the gases from some volcanoes, oil wells and coal mines. It may be liberated as a product of decomposition of organic matter. It is an important gaseous raw material used in many chemical and petroleum industries. Many metals absorb hydrogen, among which Palladium is one of the good examples. Gaseous hydrogen is shipped by truck, tanks or barge. The storage of hydrogen in the form of metal hydrides is getting increased interest as these can store hydrogen at moderate pressure, **2 MPa**, instead of storing in hydrogen cylinders at higher pressure, **14 MPa**. The common hydrides are iron-titanium, magnesium-nickel, lanthanum-nickel etc.

❖ Hydrogen gas production

A number of methods are available to prepare hydrogen gas. The choice of method is dependent on the factors like, quantity of hydrogen required, extent of purity, availability and cost of raw materials. Among the processes of hydrogen gas preparation, the following are the most used methods.

1) Electrolytic method
2) Steam reforming
3) Partial oxidation
4) Coal gasification
5) Dissociation of ammonia

- **Electrolytic method**

A dilute aqueous solution of acid or alkali is decomposed by passing direct current through them to high purity hydrogen (99.7%) and oxygen gas by the Electrolytic method.

$$2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g) \quad \cdot H= +569\ kJ$$

Electrolysis is done in a photovoltaic cell using iron cathode and nickel anode with an asbestos diaphragm separating the cells into two compartments. A 15% sodium hydroxide solution is used to electrolyze at temperature of about **$60\text{-}70^0C$**. Two types of cells are mainly used, one is bipolar or filter-press type and another one is uni-polar or tank type. The former one is such that each plate acts as an individual cell where, in the second one, two anode compartments are separated by a cathode compartment. Except dilute alkali solution, dilute acid or brine solutions may also be used in electrolysis process for production of hydrogen.

- **Steam reforming**

Steam reforming is the most economic and efficient technology among many other techniques of hydrogen preparation and it uses a wide range of hydrocarbon feed stocks. The product gas is a mixture of hydrogen and carbon monoxide which is collectively called synthesis gas. The feed materials include natural gas, liquid gas or naphtha which is endothermally converted into synthesis gas with steam in catalytic tube reactors. The heat in flue gas produced is used for the steam generation. The hydro carbon feed is preheated in coils in the waste heat section of the reformer, and sulfur is removed over a zinc oxide catalyst. The desulfurized feed is mixed with superheated process steam and this mixture is further preheated before entering to the tubular reformer. The tubes are arranged in vertical manner, heated from outside and the gas mixture flows from top to bottom through tubes. While flowing through the tubes, the hydrocarbon and steam mixture reacts together, forming hydrogen and carbon monoxide according to the following reactions:

$$C_nH_m + n\,H_2O \leftrightarrow n\,CO + \frac{n+m}{2}\,H_2 \qquad (1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

A higher steam to hydrocarbon ratio which is more than the theoretical one, is maintained to minimize the methane content and simultaneously maximizing the H2 yield in the synthesis gas. High steam to hydrocarbon ratio also prevents the formation of elemental carbon which may deposit on the catalyst. The reactions are endothermic, hence heat is supplied externally which is done by firing burners. The burners for the firing are arranged on the ceiling of the firing area between the tube rows and fire vertically downward. The flue gas is then cooled down in a convection zone, generating steam.

Nickel is the typical steam reforming catalyst. Sintering is an important cause of deactivation of nickel-containing steam reforming catalysts. The most important parameters are the temperature and the atmosphere in contact with the catalyst.

- **Partial oxidation**

Partial oxidation is the second-most important process for preparation of hydrogen after steam reforming. The feed stocks which can be used are natural gas, refinery gases or other hydrocarbon gases, but the chief advantage of this process is the utilization of liquid hydrocarbon feed stocks such as gas oil, diesel and even heavy fuel oil. This is a non-catalytic partial combustion of hydrocarbon feed with oxygen in presence of steam at **1300-1500^{0}C** temperature range. The reaction is exothermic. There are several advantages of partial oxidation. It is a simple operation with very little maintenance.

- **Coal gasification**

Synthesis gas is produced by reacting pulverized coal with oxygen and steam under high pressures and temperatures. Synthesis gas is a mixture of carbon monoxide, carbon dioxide, hydrogen as well as small amounts of some other gases and particles. Cooling and cleaning of synthesis gas remove the other gases and particles, leaving only carbon monoxide, carbon dioxide and hydrogen. . During syngas cleaning, mercury, sulfur, trace contaminants, and particulate matter are removed. The carbon monoxide in the gas mixture is reacted with steam via the water-gas shift reaction to produce additional hydrogen and carbon dioxide in a shift reactor. Hydrogen is removed by a separation system, and the highly concentrated CO_2 stream can subsequently be captured and sequestered.

- **Ammonia dissociation**

Cracking or dissociation of ammonia at high temperature produces one volume nitrogen and three volumes hydrogen. As nitrogen is an inert gas, hence, this gas mixture can be used as such for hydrogenation in industry. Liquid ammonia is vaporized from the cylinder and heated at about **870^{0}C**, passing over a catalyst, mainly nickel on alumina. The product gases are cooled in a heat exchanger by heating the reactant gas, ammonia.

- **Acetylene**

Acetylene is a combustible gas having a distinctive odour. The gas becomes explosive when it is liquefied, compressed, heated, or mixed with air; hence special precautions are taken in handling this gas. The common use of acetylene is in the preparation of various organic chemicals. One of these chemicals is 1,4-butanediol, which is widely used in the preparation of polyurethane and polyester plastics. Another important use of acetylene is in the oxy-acetylene welding and metal cutting. Acetylene black is a product from acetylene which is used in dry-cell batteries. One new application is the conversion of acetylene to ethylene for use in making a variety of polyethylene plastics.

- **Methods of preparation**

Acetylene is manufactured by two processes; one is chemical process where calcium carbide reacts with water to produce acetylene gas and calcium carbonate slurry, called **hydrated lime**.

The chemical reaction may be written as

$$\mathbf{CaC_2 + 2\,H_2\,O \rightarrow C_2H_2 + Ca(OH)_2 \;\cdot H = -129\ kJ/mole}$$

A considerable amount of heat is produced in this reaction, which must be removed to prevent explosion of acetylene gas at high temperature. Heat removal is done by two processes, one is wet process and another one is dry process. In wet process, either calcium carbide is added to water or water is added to calcium carbide. This type is called wet process because an excess amount of water is used to absorb the heat of the reaction. In dry process, a limited amount of water is used, which then evaporates as it absorbs the heat.

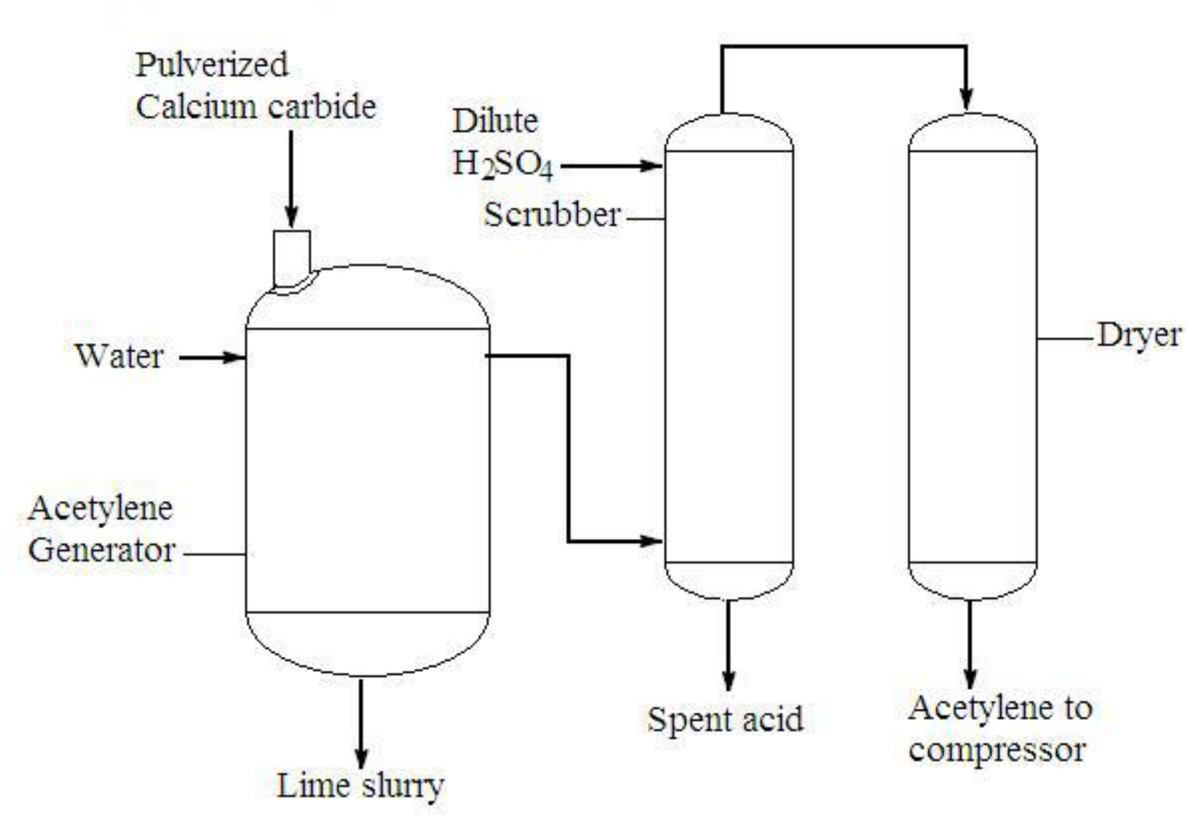


Fig.24. Acetylene generator

Fig.24. shows a schematic view of acetylene generation unit. The process starts with preparation of calcium carbide by the reaction of lime and coke in an electric arc furnace. The carbon monoxide gas

produced is removed and molten calcium carbide is recovered. Calcium carbide is solidified and round under nitrogen atmosphere to avoid explosion of acetylene produced by the moist air coming in contact with the calcium carbide. Pulverized **CaC_2** is introduced in an acetylene gas generator through a hopper at the top of it and water is added. In the wet process, sufficient quantity of water is added to remove calcium hydroxide formed in the reaction as lime slurry. The temperature should be kept below **90^0C** and pressure is within 2 atm. In the dry process, 1:1 quantity by weight of water to **CaC_2** is used. This water is removed by the heat of reaction to produce acetylene.

The cooler condenser cools the acetylene gas from the generator, which is hot along with moisture and other gaseous impurities. The impurities are traces of ammonia, sulfides and phosgene which are scrubbed by dilute H_2SO_4 solution. The gas is then again purified and dried with iron oxide and alumina or silica gel.

❖ Other processes for C_2H_2 generation

Other processes use different hydrocarbons such as crude oil and naphtha. Even coal is also used as raw materials. This is a thermal cracking process in which the raw materials are converted into hydrogen, carbon monoxide, carbon dioxide and acetylene. There are several variations of this process which depends on the raw materials used and the method of heat generation. Electric arc furnace is used for some cracking processes to heat the raw materials, while others use a combustion chamber where heat is provided by burning a part of the hydrocarbons. Steam cracking of ethylene is another process to generate acetylene as a side product. The process of producing acetylene from natural gas using combustion chamber is described below.

The chemical reaction for converting methane into acetylene and hydrogen may be written as

$$2\,CH_4 \rightarrow C_2H_2 + 3\,H_2$$

Natural gas, which is mostly methane, is preheated to about **650^0C** for the purpose of its self-ignition once it reaches the burner and this requires less oxygen for combustion. This hot gas passes through a narrow tube, called venture and at this stage oxygen is mixed to the gas. The gas mixture then passes through a diffuser, which makes a desired speed of the gas mixture. This is very important and critical. If the velocity is too high, the incoming gas will blow out the flame in the burner. If the velocity is too low, the flame can flash back and ignite the gas before it reaches the burner. After the diffuser, the gas mixture comes to the burner which comprises of more than 100 narrow channels. The gas flows through these channel and self-ignites to raise the temperature of the gas up to **1500^0C**.

Here some oxygen is also added. After the burner, reaction space comes, where the burning methane is converted to acetylene. The whole process is very fast, the time required is only some milliseconds. After the reaction, the burning gas is quickly quenched with water sprays. The cooled gas contains a large amount of carbon monoxide, carbon dioxide, hydrogen and unreacted methane along with acetylene. Some carbon soot is also formed. The gas passes through a water scrubber, which removes much of the carbon soot. In the second scrubber, N-methylpyrrolidinone solvent is used to absorb acetylene from the gas mixtures. The solvent is pumped into a separation tower where acetylene is boiled out of the solvent and is drawn off at the top of the tower as a gas, while the solvent is drawn out of the bottom.

- **Handling and safety**

Because of its explosive nature, acetylene must be stored and handled with utmost care. In the chemical plants where acetylene is needed, it is produced very near to its point of consumption and is transported through a very short pipeline at low pressure. For use in oxy-acetylene welding purpose, acetylene must be stored in a special cylinder where an absorbent, like diatomaceous earth and a small amount of acetone is kept. At the cylinder pressure, **300 psi**, acetylene is dissolved in acetone and this dissolution makes acetylene to lose its explosive power. When pressure is released by opening the cylinder valve, some acetylene vaporizes and comes out through the tube connected to the cylinder for welding or cutting torch.

❖ Coal gas

Coal gas is produced as a byproduct in high temperature carbonization of coal for making coke. Coal gas can be recovered from a byproduct coke oven. This gas is produced due to the secondary cracking reaction of gases and vapors of carbonization during coke making process and the typical composition of coal gas is methane, hydrogen, carbon monoxide, carbon dioxide, nitrogen, some higher hydrocarbon gases and a little amount of oxygen. Hydrogen comprises more than 50% of the gas composition. Hence coal gas is a good source of hydrogen for the synthesis of making ammonia in fertilizer plant. Hydrogen is also required for methanol production. Hydrocarbons and hydrogen can be recovered by compression and liquefaction. More hydrogen can be obtained from hydrocarbons by partial oxidation process. In addition to the mentioned gaseous components, coal gas may also contain some traces of objectionable impurities, such as **ammonia, tar, HCN, CS_2** and **H_2S**. **<u>These should be removed from coal gas</u>**.

This removal is done by the following ways:

Dilute ammonia is removed by scrubbing the gas in a scrubber. The gaseous impurities are removed in different ways in the gas purification section. **Carbon disulphide** is removed by reacting with hydrogen on a nickel catalyst by the following reaction,

$\mathbf{CS_2 + 2H_2 \rightarrow 2H_2S + C}$

$\mathbf{CS_2 + 4H_2 \rightarrow 2H_2S + CH_4}$

Next, the gas is treated with iron oxide to remove hydrogen sulphide and hydrogen cyanide according to the following reactions,

$\mathbf{Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O}$

$\mathbf{Fe_2O_3 + 6HCN \rightarrow 2FeC_3N_3 + 3H_2O}$

$\mathbf{FeC_3N_3}$ is called **Prussian blue**, it is a **valuable pigment**, which is washed out by water. Coal tar in the gas is removed in a separator. Benzene, naphthalene and other valuable organic materials are distilled from tar and the remaining thick liquid is used for paving purpose.

❖ Refinery gases

The mixture of gases generated during different refinery operations are said refinery gases. The gas composition varies depending on the type of crude from which they originate. The gas components are mainly methane, ethane, ethylene, propane, propylene, butane, butylenes etc. After the crude oil is taken out from underground, it is subjected to different operations to refine and get different fractions from it. The stage includes mainly distillation, atmospheric and vacuum. During this process, different gases are obtained from overhead which comprises refinery gas mixture. After distillations, the petroleum cuts are subjected to a number of secondary processes, such as, cracking, reforming, visbreaking, coking etc. These processes also produce refinery gasses of the said composition. The quantity of gas produced in a particular operation is dependent on the process conditions. Refinery gas can be used as a fuel gas. It is absorbed are as a feed stock in petrochemical industries, after separation of the components in a cold separation process. Ethylene, propylene, butylenes are the first generation petrochemical feed stock. Propane, propylene and butane, butylenes mixtures can be bottled at high pressure in liquid form and used as liquefied petroleum gas.

❖ Blast furnace gas

Blast furnace gas is a by-product of the reduction reaction of iron ore with coke in the blast furnace, to produce metallic iron. The calorific value of this gas is very low, about **1000 kcal/m^3**. The reason for the low calorific value is that, the gas contains about **60%** nitrogen, **18-20%** carbon dioxide and rest is mainly carbon monoxide with a little oxygen. The first two gases do not contribute to the calorific value and occupies major volume. The combustion gases in the blast furnace are produced at the combustion zone of the furnace which is at the bottom of it. During ascending through the descending charge of coke, carbon reduces carbon dioxide to carbon monoxide and steam is decomposed into hydrogen and carbon monoxide. Iron oxide is reduced by carbon monoxide and partly by hydrogen. After all these reactions, the produced gases ultimately come out through the upper part of the furnace at high temperature, around **150 to 200^{0}C**. This gas is blast furnace gas. This gas contains lots of dust, about **20-30 g/m^3** and is usually cleaned by dust settlers, cyclones or electrostatic precipitators before use. The required quality of blast furnace for use in industrial burners and gas engines are **0.5** and **0.01 g/m^3** dust content.

Blast furnace gas is mainly used as a fuel in admixture with a richer calorific value fuel gas, such as coal gas or coke oven gas. About one-third of blast furnace gas is used for preheating air used in blast furnace itself and the remaining two-third is utilized in boilers or in gas engines. It is also used as a fuel in burning a special type of stove, called Cowper's stove to preheat the furnace.

❖ Oil gasification

Gasification of oil is done to produce hydrocarbon gases or synthesis gas. The processes followed for gasification are cracking, removal of carbon in the form of coke or hydrogenation, which means, either fragmentation of hydrocarbon chains or change in **C/H** ratio. The feed stocks used for gasification are light distillate, middle distillate or heavy distillates. The gasification is done by supplying air and steam to the oil to convert it into carbon monoxide and hydrogen according to the following reaction,

$$\mathbf{C_nH_m + \frac{n}{2}\, O_2 \leftrightarrow n\, CO + \frac{m}{2}\, H_2} \qquad \textbf{(a)}$$

$$\textbf{and, } \mathbf{C_nH_m + n\, H_2O \leftrightarrow n\, CO + (n + \frac{m}{2})\, H_2} \qquad \textbf{(b)}$$

Reactions (a) and (b) are partial oxidation and steam reforming respectively.

The cracking reaction of decane is,

$\mathbf{C_{10}H_{22} \rightarrow C_2H_4 + C_8H_{18}}$ **(c)**

The light hydrocarbon gases generated in cracking are used as gaseous fuel. Cracking and steam reforming reactions are highly endothermic, while partial oxidation is exothermic.

❖ Bio gas

The gas produced by anaerobic bacterial digestion or fermentation of organic matter is called biogas. The organic matter may be agricultural waste, animal dung, manure, sewage sludge, municipal solid waste, biodegradable waste etc. Biogas is a fuel gas, a mixture consisting of 65% methane and 35% carbon dioxide. Depending on the source of the gas, its composition varies.

The presence of $\mathbf{H_2S}$, makes biogas very corrosive and this requires pretreatment of biogas before its use.

Biogas production by anaerobic digestion is popular for treating biodegradable waste. Biogas is a cleaner fuel than coal, as the methane in biogas produces more energy with less emissions of carbon dioxide compared to coal.

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Module-3

Synthetic Fuels

❖ Coal liquefaction

Coal liquefaction is a process where coal is converted into liquid fuels, mainly to provide substitutes for petroleum products, which may be either used directly as fuel or converted into chemicals or other liquid fuels. Coal liquefaction processes were first developed in the early 20th century. The crude petroleum rich countries may not need this process for fulfilling their requirement of liquid fuel but the countries which are lacking of crude but have a good reserve of solid fuel like coal, a large scale applications of coal liquefaction process is entertained. The few countries, where this process is mainly running are Germany (during **World War II**) and South Africa since the year **1960**s. USA is also running coal to liquid fuel plant successfully. A plant using more than six million tons of coal annually could produce more than 3.6 million barrels of diesel and napththa. China has expended fifteen billion dollar for coal to diesel fuel conversion plant with the aim of replacing **10%** of its oil import with coal converted liquid oils by the year **2013**. The threat of depletion of conventional oil sources is another major reason for renewed interest in the production of oil substitutes from coal since last three decades.

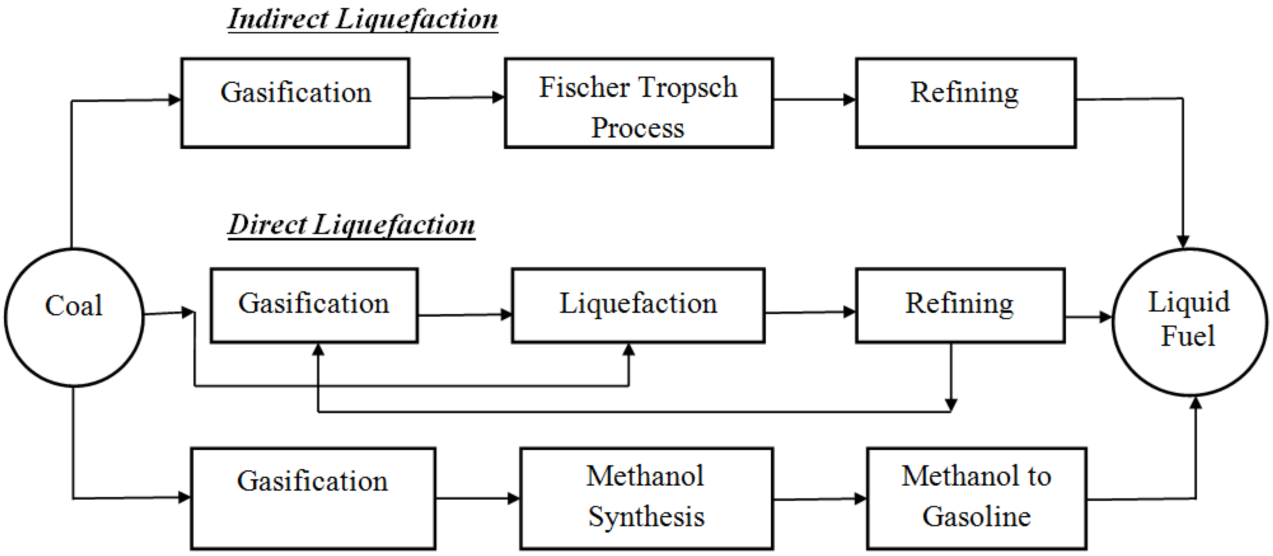


Fig. 25. Different routes of coal liquefaction

Hydrocarbon type liquid fuels are obtained from solid fuel like coal by the following routes mainly:

- Hydrogenation of coal
- Solvent extraction of coal and hydrogenation of coal extracts
- Refining of tar and oil obtained from carbonization of various soild fuels and oil shales
- Gasification of solid fuels into synthesis gas and conversion of the gas into liquid fuels and chemicals.

The block diagram (**Fig. 25.**) shows the options for coal to liquid conversion plants.

Coal liquefaction can be achieved either by direct or indirect processes. The difference between these two processes lies in that, the indirect liquefaction process needs to go through gasification first, while, direct liquefaction process involves producing partially refined synthetic oil from coal. It is said by the technologists that, indirect liquefaction is more efficient than direct coal liquefaction techniques which are currently available.

❖ Direct liquefaction

Direct coal liquefaction was developed by Friedrich Bergius and it was started commercially in Germany near World War II, to meet the huge demand of liquid fuel at that time. Bergius process was modified and extended to fulfill today's demand of liquid fuel. The coal is ground so that it can be mixed into coal derived heavy oil recycled from the process to form a coal-oil slurry feed. The slurry containing **30-50%** coal is then heated in a reactor to about **450°C** in a hydrogen atmosphere between **14-22 MPa** pressures for about one hour. Different catalyst used are tungsten or molybdenum sulfides, tin or nickel oleate. The reaction produces heavy oil, middle oil, gasoline and gases. One tonne of coal yields about one-half tonne of liquids. Processes have been developed to use coals from low rank lignites to high volatile bituminous coals. Higher-rank coals are less reactive and anthracites are essentially non-reactive.

The liquids produced have molecular structures similar to those found in aromatic compounds and need further upgrading to produce specification fuels such as gasoline and fuel oil.

Direct coal liquefaction is suitable for a wide range of feeds:

- High volatile bituminous coals

- Sub-bituminous coals with low ash
- Lignites with low ash

Direct liquefaction is of two types, single stage and two stage processes. In single-stage direct liquefaction process, one primary reactor is used to get distillates. Here a hydrotreating reactor is also joined along with the primary reactor to improve the quality of the distillate. The technology developers are

- H-Coal (HRI, USA)
- Exxon donor solvent (Exxon, USA)
- SRC-1 and II (Gulf Oil, USA)
- Conoco zinc chloride (Conoco, USA)
- Kohleoel (Ruhrkohle, Germany)
- NEDOL (NEDO, Japan)

Two reactors in series are used in two-stage direct liquefaction process. In the first stage, coal dissolution is done where the process is operated either without a catalyst or with a low-activity disposable catalyst. The heavy coal liquids produced in the first reactor are hydrotreated in the second stage in the presence of a high-activity catalyst to produce desired distillate. The process and technology developers include

- Catalytic two-stage liquefaction (US DOE and HTI, USA)
- Liquid solvent extraction (British Coal Corporation, UK)
- Brown coal liquefaction (NEDO, Japan)
- Consol synthetic fuel (Consol, USA)
- Lummus (Lummus, USA)

Among the different commercial processes, Exxon donor solvent process (EDS) and H-coal process are discussed here.

- **EDS (Exxon Donor Solvent) process**

In this process coal slurry is prepared using a recycled solvent and the slurry is mixed with $\mathbf{H_2}$, preheated and fed to a simple up-flow tubular reactor. The reactor operates at **425-450 ºC** and **2575 psig** pressure. It is a non-catalytic process. The ligher product naphtha, a middle distillate and a heavy distillate product are obtained. Heavy distillate mixed with some middle distillate forms the recycle solvent. The recycle solvent is hydrogenated in a fixed-bed catalytic reactor operated at **370 ºC** and **1600 psig H_2** pressure depending on the extent of hydrogenation, where either nickel-molybdenum or cobalt-molybdenum on alumina support is used as a catalyst. A flow diagram of EDS process is described in **Fig. 26**.

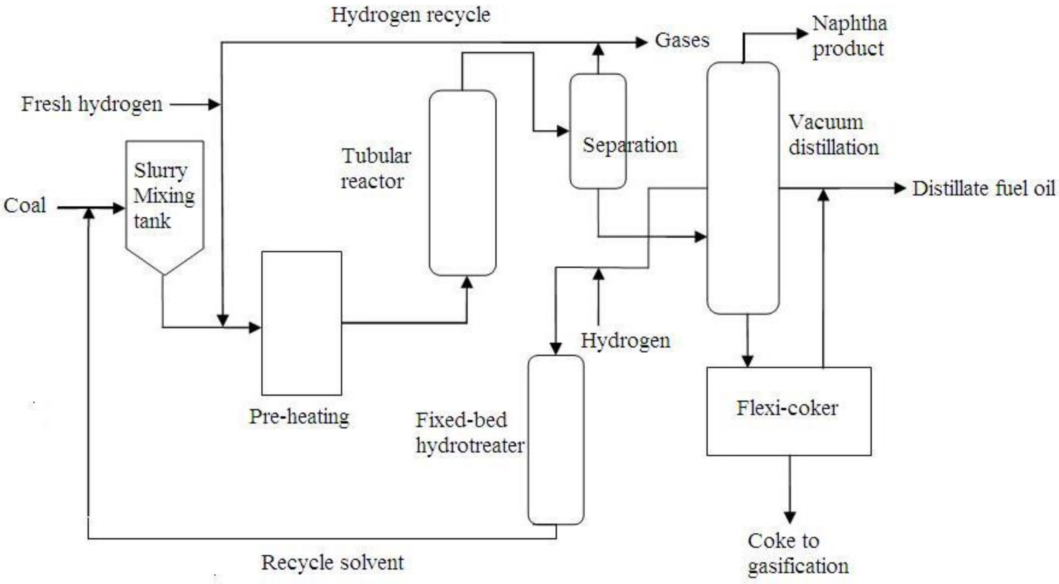


Fig. 26. Flow diagram of EDS process

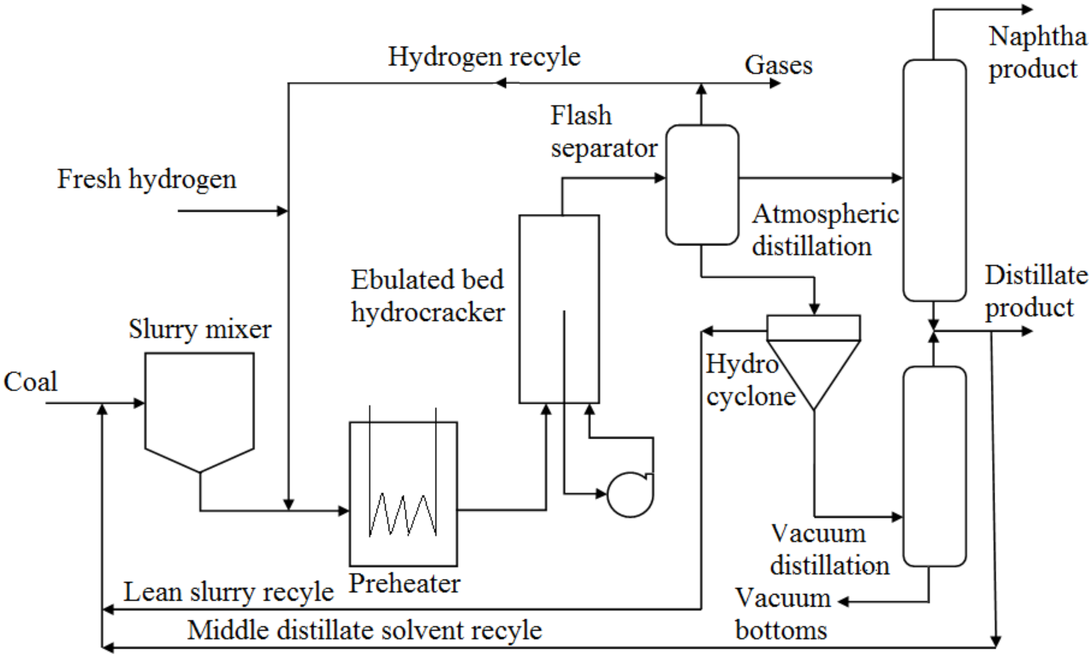


Fig. 27. Process flow diagram of H-Coal process

❖ H-coal process

In this process, coal slurry is prepared with a recycle solvent that consists of a mixture of heavy and middle distillates obtained by product fractionation and solids containing hydrocracker product. $\mathbf{H_2}$ is added to the slurry, the mixture is preheated and fed to an ebullated bed hydrocracker, which is the distinguishing feature of the process. The reaction conditions are : temperature **425-455 ºC** and H_2 pressure **2900 psig**. The catalyst used is either **Ni-Mo** or **Co-Mo** supported on alumina. The catalyst is fluidized by $\mathbf{H_2}$ and a pumped internal recycle stream. This recycle stream contains unreacted coal solids.

H-coal process is described in **Fig. 27** in the form of a flow diagram. The advantages of ebullated bed reactor over fixed-bed reactors are that, the reactor contents are well mixed and temperature can be monitored and controlled in better way in the previous one.

❖ Indirect liquefaction

Indirect liquefaction (ICL) of coal is the process for production of fuels with an intermediate step of production of synthesis gas (syngas) by gasification of coal. The principal constituents of syngas are carbon monoxide and hydrogen, which can be processed chemically in further steps to produce a variety of different chemicals and fuels. Chemicals and fuels that can be made by **ICL** include methanol ($\mathbf{CH_3OH}$), dimethyl ether ($\mathbf{CH_3OCH_3}$) and Fischer-Tropsch diesel- or gasoline-like fuels, and hydrogen ($\mathbf{H_2}$). **ICL** is practiced commercially in South Africa (for Fischer-Tropsch fuels) for fuel production.

The production of methanol by **ICL** processes, primarily for the use as a feedstock for different chemicals as well a vehicle fuel, is already commercially established. Production of dimethyl ether by **ICL** is also drawing considerable interest as it is a potential feedstock of chemicals, can be used in compression ignition engine along with diesel for its high cetane rating and nonsooting nature, can be used as an alternative fuel for **LPG** because of its high calorific value and non-toxic character.

The process of **ICL** involves two steps. The first step is the complete breakdown of coal structure by gasification process to produce mainly syngas. Sulfur-bearing compounds are removed at this step. Gasification products are reacted in the presence of a catalyst at definite temperature and pressure. The synthetic liquid products include paraffins, olefins and alcohol, mainly methanol, depending on the catalyst selected and the reaction conditions used.

❖ Fischer-Tropsch (FT) Synthesis

Fischer-Tropsch (FT) synthesis, named after the German inventors, Franz Fischer and Hans Tropsch in the 1920s, is a well-known catalytic process to produce liquid transportation fuels from syngas. During World War II, **FT** synthesis process provided the liquid hydrocarbon fuels required for the German in the war. After that, great efforts were made to refine and develop the new technology for **FT** process, including catalyst development and reactor design. Depending on the source of the syngas, the technology is often termed to as coal-to-liquids **(CTL)** and/or gas-to-liquids **(GTL)**.

In the FT process, carbon monoxide **(CO)** and hydrogen **(H_2)** in syngas react catalytically to convert into hydrocarbons of a series of molecular weights according to the following equation:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_n\ H_{(2n+2)} + n\ H_2O$$

Where n is an integer. Thus, when **n=1**, the reaction represents the formation of methane, which is considered an undesirable byproduct. The main aim of Fischer-Tropsch process is to maximize the formation of hydrocarbons in the range of liquid fuels, which are higher value products, by using suitable reaction conditions and catalysts. Some other side reactions occur in this process, among which the water-gas-shift reaction is the main.

$$CO + H_2O \rightarrow H_2 + CO_2$$

FT process produces hydrocarbons ranging from methane to higher molecular paraffins and olefins, along with small amounts of organic alcohols and acids, depending on the reaction conditions and catalyst used. The **FT** reaction is actually a condensation polymerization reaction of **CO**. The most common catalysts used are iron, cobalt, nickel or ruthenium. The main focus of **FT** process is the production of high molecular weight linear alkanes and diesel fuel. In addition to the active metal part of the catalyst, they typically contain a number of promoters, including potassium and copper, as well as high surface area binders/supports such as silica and/or alumina. As the **FT** catalysts may be poisoned by the sulfur compounds present in the syngas, hence the gas should be made free of sulfur compounds before it is introduced to the reactor. Originally cobult was used as the catalyst for **FT** process, but it is highly sensitive to the sulfur compounds compared to **Fe** catalysts. Hence, syngas obtained from high sulfur coal is treated with iron catalysts as those are not much sensitive towards sulfur. **FT** reaction is highly exothermic and so, the control of the reaction temperature is a critical factor. Three types of reactors, fixed bed, fluidized bed and slurry bed may be used commercially in the process. Fixed bed reactor is known as Arge reactor, which was developed by Lurgi and Ruhrchemie. Now most of the fixed bed reactors are replaced by slurry bed reactors, developed by Exxon and Shell. Fluidised bed reactor was developed by Kellog.

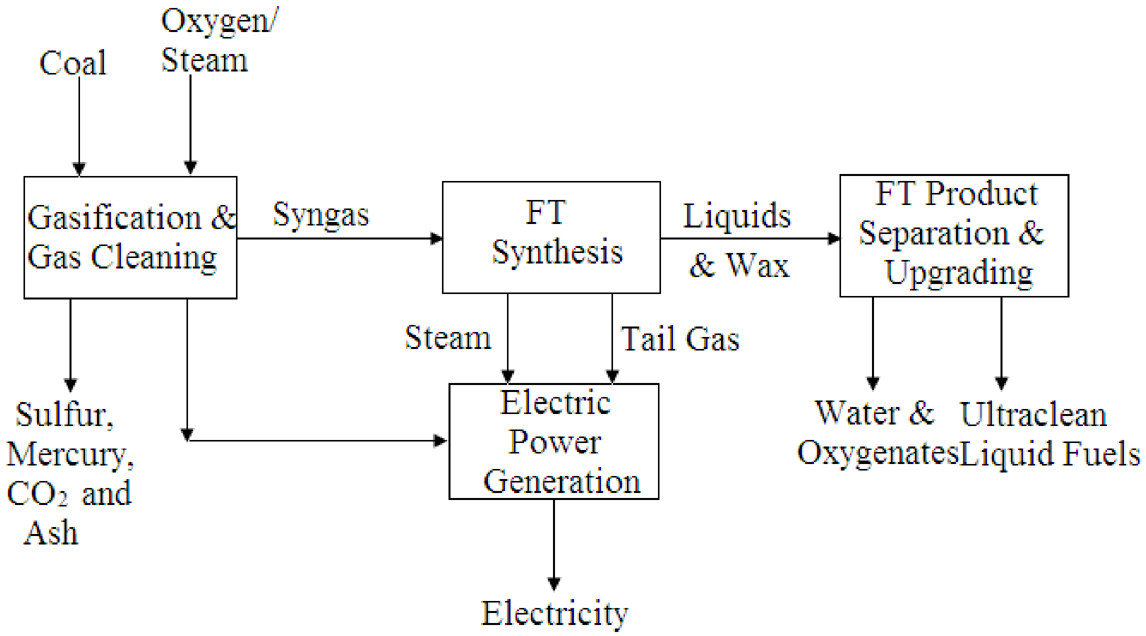


Fig. 28. Fischer-Tropsch process flow diagram.

Fig. 28 shows a process flow diagram of **FT** process. The temperature range used in the **FT** process is **150-350°C**. High temperature **FT** process **(300-350°C)** uses iron-based catalyst, whereas low temperature **FT** process **(>300°C)** uses cobalt-based catalyst. Although higher temperature shows faster reaction rate, yet, it favours methane production. For this reason, a moderate temperature range is most desirable for the process. High temperature **FT** process is extensively used in Sasol plant, South Africa, in their coal to liquid **(CTL)** plants. Low temperature gas to liquid **(GTL)** plant is commercialized in Malaysia, built by Shell. Typical pressures range used is one to several tens of atmospheres.

❖ Methanol to Gasoline (MTG) process

Methanol to Gasoline process (**MTG**) was discovered by Exxon-Mobil scientists in the **1970'**s. Both the Fisher-Tropsch and **MTG** processes convert coal into synthesis gas before converting it to the final liquid products. However, there are some basic differences between them in terms of product distribution. The Fisher-Tropsch process produces a broad range of straight-chain paraffinic hydrocarbons that require upgrading to produce commercial quality gasoline, jet fuel and diesel. In contrary, **MTG** selectively converts methanol to one liquid product, a very low sulfur and low benzene regular octane gasoline.

After coal is gasified to produce synthesis gas, methanol is produced from syngas in a methanol convertor reactor operated at **220-275°C** and **50-100 bar** pressure on **$Cu/ZnO/Al_2O_3$** catalyst. After the production of methanol, it is fed to a fixed bed reactor system where in the first part, methanol is converted to an equilibrium mixture of methanol, dimethyl ether, and water.

In the second step, the equilibrium mixture is mixed with recycle gas and passed over specially designed **ZSM-5** catalyst to produce hydrocarbons and water. Most of the hydrocarbon products are in the gasoline range. Most of the gas is recycled to the **ZSM-5** reactor.

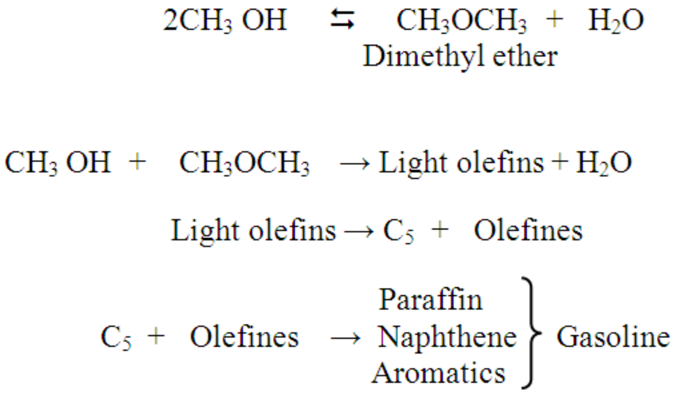


Fig. 29. Reactions of MTG process

MTG reactor effluent is separated into gas, raw gasoline and water. Raw gasoline is separated into **LPG**, light gasoline and heavy gasoline. Heavy gasoline is hydro-treated to reduce durene content. Heavy and light gasolines are re-combined into finished MTG gasoline. **MTG** process is exothermic in nature. The **Fig. 29** describes the reactions involved in production gasoline via **MTG** process.

❖ Indian Scenario

Oil India Limited (**OIL**) has carried out an elaborate study regarding the conversion of various shales and coals from north-east India into liquid fuels. It has been found that high sulfur, low ash containing bituminous coal of **NE** India is quite suitable for liquefaction. **OIL** embarked a coal liquefaction project based on Hydrocarbon research Incorporation's Coal-Oil processing technology and set up a **25 kg/day** pilot plant in Duliajan, Assam. The characteristic properties of coal used are, ash: **2-10 wt%**, volatile matter: **40-45%** and sulfur: **1.5 to 6 wt%.** The assay found that the coal reserve of around **467 MMT** may produce **200 MMT** of liquid fuel.

❖ Coal gasification

Coal gasification technology is efficiently used for converting coal to power, chemicals, fertilizers, and fuels. This gasification process is a clean technology to decompose coal into its different components in presence of steam and oxygen at high pressure and high temperature. This leads to the production of synthesis gas, which is mainly a mixture of carbon monoxide and hydrogen. Coal gasification can be utilized to produce methanol as alternative energy source.

The major applications of coal gasification are in

- Power generation
- Fertilizer
- Methanol synthesis
- Hydrogen
- Hydrocarbons

It provides the only route to convert coal to hydrogen directly. In this process, coal is combined with oxygen and steam to produce a combustible gas, waste gases, char, and ash. Coal gasification may be generally represented by reaction

$$C_mH_n + 0.5mO_2 \leftrightarrow mCO + 0.5\,n\,H_2$$

Where, '**m**' and '**n**' depends on the composition of coal. The reactions in different stages of the process are as follows:

i) $CO + H_2O \leftrightarrow CO_2 + H_2$

ii) $C + CO_2 \leftrightarrow 2\,CO$

iii) $\mathbf{C + H_2O \leftrightarrow CO + H_2}$

iv) $\mathbf{CH_4 + H_2O \leftrightarrow CO + 3H_2}$

The gasification of coal generally consists of four steps:

- Pre treatment of Coal
- Gasification
- Gas cleaning, and
- Gas beneficiation.

The process flow diagram for coal gasification is described in **Fig. 30**.

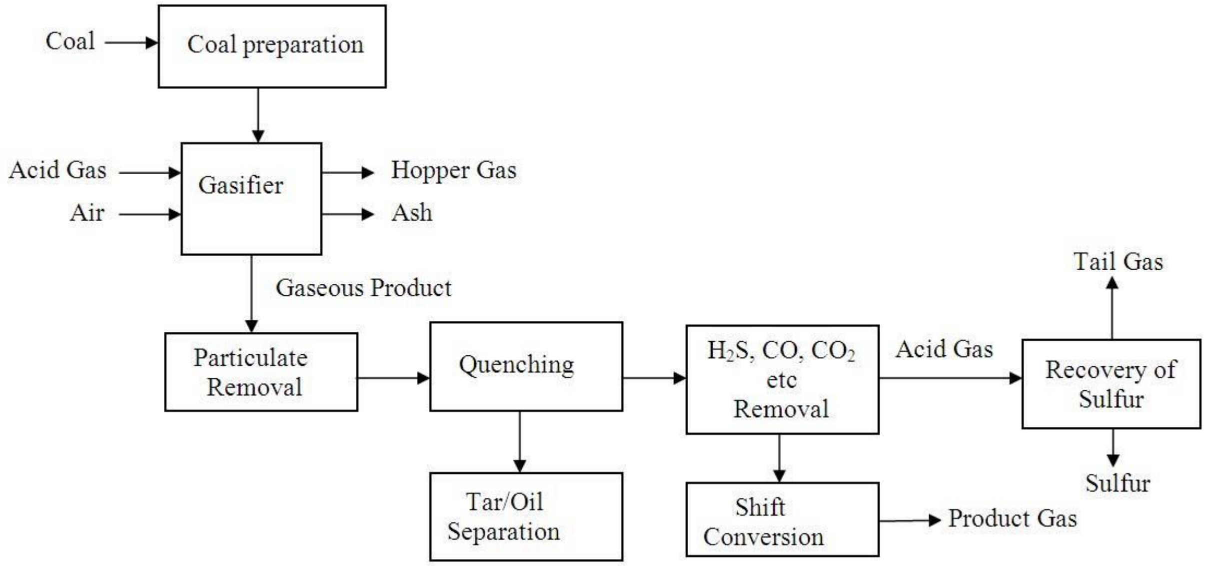


Fig.30. Coal Gasification

❖ **Selection of suitable coal for gasification**

The selection of an appropriate coal is the important step at the initial stage of coal gasification. The various sources of coal samples are analyzed and compared in terms of their costs and compositions. The comparison is generally made by the percentages of sulfur content, fixed carbon, oxygen, ash and other volatile content. The sub-bituminous coal is found to have the lowest percentage of sulfur content in comparison with lignite and bituminous coal.

One important step in the preparation of the syngas is the removal of acid gas, which can be composed of $\mathbf{H_2S}$ and $\mathbf{CO_2}$. In high temperature processes all sulfur components in the feed are converted to undesired products, such as, **H_2S** or **COS**, which are needed to be removed by acid gas removal process. Therefore, a low sulfur content coal is a desirable feed. Then ideally, the syngas mixture would have a **1:2 CO** to **H_2** ratio. Steam can also be used to produce more hydrogen by reacting it with carbon monoxide via the water-gas shift reaction for methanol synthesis:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Methanol is produced by the reaction

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

❖ Description of Gasification process

- ***Coal preparation***

In the pretreatment step, coal is first dried and crushed or pulverized for the fluid or entrained bed gasifiers. The moisture of coals should be removed by drying. Some caking coals may require partial oxidation to simplify gasifier operation. For feed to fixed bed gasifiers, briqueting of fines coal particle are required in the pretreatment process.

- ***Gasification***

The pre-treated coal is charged into the gasification reactor where it reacts with oxygen (air) and steam. The gasification reaction usually takes place at high temperatures from **800** to **1900°C** and high pressure up to **10 MPa**. When coal is burned with less than a stoichiometric quantity of air, with or without steam, the product is a low-heat-content gas, which after purification can be used as fuel gas. Using oxygen in place of air produces medium-heat-content gas. Some of **CO** must be reacted with steam by shift conversion to get additional hydrogen. The ashes from gasifier are removed as molten slag or dry condition.

Shell Coal Gasification Process is the oldest technology and it was the first commercial plant used in **1956.**

The process conditions were:

- Pressure: **20-40** bar
- Temperature: **1300 –1800** °C
- Oxygen/coal **(MAF)** ratio: 1
- Steam pressures: **30 –130** bar

❖ Purification of product gas

The gas products from the gasifier contain a mixture of different gases such as, carbon monoxide, carbon dioxide, hydrogen, methane, other organic vapours and hydrogen sulfide in different concentrations. Nitrogen is also present in gas products if air is used. Other impurities are particulates, and water vapour. The product gas is then purified prior to their combustion through the removal of particulate matters, such as, coal dust, ash and tar aerosols. The tar and oil are removed by gas quenching method, and then the acid gas is removed by solvent treatment technology. The tar and oils are condensed in the gas quenching and cooling section of the plant. Ammonia is removed from the gas in a scrubber by using either aqueous or organic liquid. Acid gases such as $\mathbf{H_2S}$, **COS**, $\mathbf{CS_2}$, **mercaptans**, and $\mathbf{CO_2}$ can be removed from gas by an acid gas removal step, where it is treated with a solvent to absorb the acid gases. Methanol may be used as a solvent to separate acid gases such as hydrogen sulfide and carbon dioxide from feed gas streams.

In the shift conversion process, $\mathbf{H_2O}$ and a portion of the **CO** catalytically react to form $\mathbf{CO_2}$ and $\mathbf{H_2}$. After passing through an absorber for $\mathbf{CO_2}$ removal, **CO** and $\mathbf{H_2}$ remain in the product gas. They are reacted in a methanation reactor to yield $\mathbf{CH_4}$ and $\mathbf{H_2O}$. Many processes are directly related with a coal gasification process, such as, oxygen plant, power and steam plant, sulfur recovery unit etc.

❖ Different Gasification Technique

Following types of Coal Gasification reactors may be used

- Fixed bed gasifier
- Moving bed gasifier
- Fluid bed gasifier
- Entrained-flow gasifiers

In the moving bed gasifier the coal bed slowly moves downwards counter currently with respect to air and is gasified. It has the lowest oxygen consumption. Moving bed gasifier can operate at the lowest temperature, which inhibits the reaction rate and increase the maintenance cost.

The fluid bed gasifier facilitates good mixing and it has low overall cost. However, the conversion rate of carbon is lower in comparison with the other two types due to some carbon lost with the ash. Also the fluid bed gasifier is appropriate for low rank coals like lignite, as opposed to sub-bituminous. In the entrained flow gasifier, the fine coal particles react with co-currently flowing steam and oxygen. Since the gasifier operates at a high temperature, a good conversion of about **99%** is obtained and the destruction of tar and oil yields a very pure syngas. However, the entrained flow gasifier has a high oxygen demand and also the high ash content in the sub-bituminous coal would increase the oxygen consumption. Overall, the entrained flow gasifier is chosen as the gasifier technology for its high carbon conversion and purity of the resulting syngas.

Both the dry and wet coal feed can be used for the entrained gasifier. For dry coal feed, it requires about **25%** less oxygen consumption and which can optimize the gas production rate. Whereas, a wet coal feed needs more oxygen consumption and it decreases the efficiency due to the evaporation of water. So, a dry coal feed is much better than a wet feed for the entrained flow gasifier to reduce the required oxygen.

Two different types of gasifiers are used in dry-coal feed gasifiers, single stage and two stage gasifiers. In single stage entrained-flow gasifier, gas with high purity is obtained. It ensures low **CO_2** and high carbon conversion, in a two-stage gasifier, there is an increase in the efficiency from single stage gasifier. The oxygen consumption is also less. Out of the types of gasifiers mentioned above, the **Noell gasifier** and the **CCP** gasifier can be considered. The **Noell gasifier** is a single stage gasifier. The **CCP** gasifier is relatively new and is advantageous because it uses air as the oxidant, which is readily available. The carbon conversion rate is **99.8%**, with a variety of coals. Other advantages include lower **NOx** and **SOx** emissions, a reduction in solid waste generated.

Nuclear Fuels

❖ Discovery of Fission

Rutherford described as the father of nuclear physics, bombarded alpha particles on Nitrogen to eject a proton and thus started the business of splitting atom in 1917. James Chadwick is credited with discovering neutron in 1932. Being neutral, it can easily penetrate the Columb barrier and interact directly with the nucleus. Enrico Fermi, considered to be one of the most brilliant physicist, postulated and succeeded in producing transuranic elements by bombarding neutrons on Uranium. However, he did not realize that he had fissioned Uranium in 1934. Otto Hahn, Fritz Strassman and Lise Meitner in 1938 conducted experiments similar to Fermi. They noticed that instead of a heavy element formation they found lighter elements in the product. They were the first ones to postulate fission and pointed the large energy that will be released. We shall see later how this energy release is made possible.

❖ Rutherford's Model

- Rutherford, based on experimentation, had proposed a model for the atom.
- It has a central positively charged nucleus consisting of protons and neutrons.
- It has electrons revolving around to make the atom neutral.
- **The charge and mass are summarised in the following table.**

	Mass	**Charge**
Proton	1.67261×10^{-24} g	$+1.67261 \times 10^{-19}$ Columbs
Electron	9.10956×10^{-28} g	-1.60219×10^{-19} Columbs
Neutron	1.67492×10^{-24} g	0

❖ Binding Energy

Binding energy of a nucleus is defined as the energy required to break a nucleus into its constituents.

- It increases with the number of nucleons in a nucleus.
- Higher the binding energy per nucleon, more stable is the nuclei.
- Iron is the most stable nuclei.
- We also note that as light elements fuse or heavy elements undergo fission, the products are more stable.

❖ Fissile Elements

- Consider the following equation

$$^{233}_{92}U + ^{1}_{0}n \rightarrow ^{234}_{92}U + \gamma(6.6MeV)$$

- 6.6 MeV is released on account of nuetron being absorbed or bound to **U-234** nucleus.
- Thus, Binding Energy of Last Neutron is **6.6 MeV**.
- Energy necessary to be supplied to induce fission is called Critical Energy for Fission.
- The binding energy of last neutron and critical energy for fission for some isotopes are listed below:

Isotope	**Critical Energy for Fission (MeV)**	**Binding Energy of Last Neutron (MeV)**
Th^{232}	**6.5**	**5.1**
U^{234}	**4.6**	**6.6**
U^{236}	**5.3**	**6.4**
U^{239}	**5.5**	**4.9**
Pu^{240}	**4.0**	**6.4**

- Thus when neutron is absorbed in $\mathbf{U^{233}}$ the neutron deposits its binding energy in the compound nucleus $\mathbf{(U^{234})}$, which is more than what is required to make $\mathbf{U^{234}}$ fission. Hence it splits spontaneously.
- Those elements which can be fissioned by zero energy neutrons are called fissile elements.
- Thus $\mathbf{U^{233}}$, $\mathbf{U^{235}}$ and $\mathbf{Pu^{239}}$ are fissile elements.
- On the other hand, $\mathbf{Th^{232}}$ and $\mathbf{U^{238}}$ need neutrons with **1.4 MeV** and **0.6 MeV** respectively for inducing fission. Hence these are called fissionable nuclei.
- Natural Uranium has **99.3%** of $\mathbf{U^{238}}$ and **0.7%** of $\mathbf{U^{235}}$.
- $\mathbf{U^{235}}$ is the only naturally occuring fissile element.

❖ Prompt Neutron Spectrum

- Nutrons released from fission have an average Energy = **1.98 MeV**.
- A large fraction of neutron is above the threshold energy of **0.6 MeV** (refer table in previous page) needed to fission $\mathbf{U^{238}}$.
- Thus some $\mathbf{U^{238}}$ is also directly fissioned in reactors.
- It has been noticed that as the energy of the colliding neutron is high, the probability of reaction is poor.
- This is attributed to the reduced time a neutron spends in the zone of interaction.
- Hence the probability of reaction is inversely proportional to the speed of the neutron.
- As the interaction decreases rapidly with increase in energy, and that the energy of the prompt neutrons are high, we need to slow them down.
- This is done by the use of moderator.

❖ Moderators and Coolants

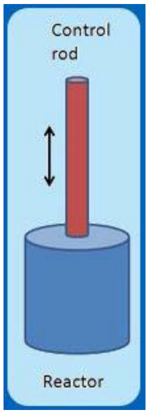
- Hydrogen in the form of water $\mathbf{(H_2O)}$ and heavy hydrogen in the form of heavy water $\mathbf{(D_2O)}$ are the most common moderators.
- In gas cooled reactors graphite **(C)** is used as the moderator.
- Coolant is employed to transport the heat generated in the core to the steam generator, where steam is generated.
- In water moderated reactors the same fluid also serves as coolant.
- There are some safety advantages if we use gas as a coolant. In such cases $\mathbf{CO_2}$ or **He** is used.

❖ Critical Size

- All neutrons produced do not get absorbed in the reactor.
- Many neutrons leak out of the reactor.
- To keep the neutron population steady in a reactor we need to produce more neutrons than what is absorbed in fuel.
- As the number of neutrons produced depends on the volume and number of neutrons leaking is proportional to surface area, there exists a minimum size below which the reactor cannot operate (due to excess leakage). This is called the critical size.
- Thus, for a reactor to operate we need a critical size.
- This size depends on the concentration of the fissile elements.
- The size increases with the reduction in concentration.
- Thus conceptually, as fuel burns out we need to increase the size, which is impractical.
- To overcome this, the size of the reactor is increased to begin with and to compensate for the excess production, neutron absorbers are used.
- As fuel burns out the absorbers are gradually removed.

❖ Control of Nuclear Reactors

- The process of power addition or reduction is done by insertion or removal of control rods.
- Originally when the fuel is fresh and the reactor is not operating, these rods are fully in.
- To start the reactor, these are slowly pulled out and the rector begins operation when the rods are out by a small amount.
- As the fissile elements deplete, to compensate for them these are continuously pulled out.
- When they get pulled out completely, then reactor is stopped and fresh fuel added.



❖ **Fast Breeders**

- We shall show later in the course that we get around 2 effective neutrons from fission induced by fully moderated neutrons.
- However, if we do not fully slow down and allow the neutron to induce fission at higher speeds, we get more effective neutrons per fission.
- While only one neutron is required to get the reactor operating steadily, the excess neutrons can be used to produce fresh fuel.
- This is called breeding.
- Since neutrons are not fully slowed down, it is called fast breeder.
- Such rectors are usually cooled by sodium.

❖ **Power Reactors**

Reactors used for power generation are called power reactors. These can be further classified as follows:

- Based on the coolant: Light Water Reactor (**light water as coolant**), Heavy Water Reactor (**heavy water as coolant**), Gas-Cooled Reactor (**CO_2/He as coolant**), Liquid Metal Cooled Reactor (liquid sodium as coolant)
- Based on the operating pressure: Pressurized Water Reactor, Boiling Water Reactor
- Based on the neutron energies: Thermal reactor, Fast reactor
- Based on the moderator: Graphite-moderated, Water-moderated
- Based on the capability to produce more fuel than they consume: Breeder reactor

❖ **Some of the characteristics of nuclear power reactors are summarized in the following Table:**

Type	**Moderator**	**Coolant**	**Pressure (bar)**	**Maximum Temp (C)**	**Eff. %**
Pressurized	Light Water	Light Water	150	320	33

Water Reactor					
Boiling Water Reactor	Light Water	Light Water	70	250	33
Pressurized Heavy Water Reactor	Heavy Water	Heavy Water	80	320	32
Gas Cooled Reactor	Graphite	Carbon dioxide	15	410	35
High Temperature Gas Reactor	Graphite	Helium	45	800	45
Liquid Metal Fast Reactor	-------	Sodium	1	580	42

Pressurized Water Reactor (PWR)

As the name of the reactor implies, the pressurized water reactor uses light water at high pressure as the coolant. Typically the operating pressure is about**155 bar (~ 153 atm)**. The pressurized water reactor utilizes enriched uranium (with **U-235** content about **3%**) as the fuel and light water as both moderator and coolant. Compared to Heavy water, the moderating capability of light water is less. Hence enriched uranium is required to sustain the fission when light water is used as moderator. A schematic diagram of a power plant utilizing Pressurized Water Reactor is shown in **Fig. 31**.

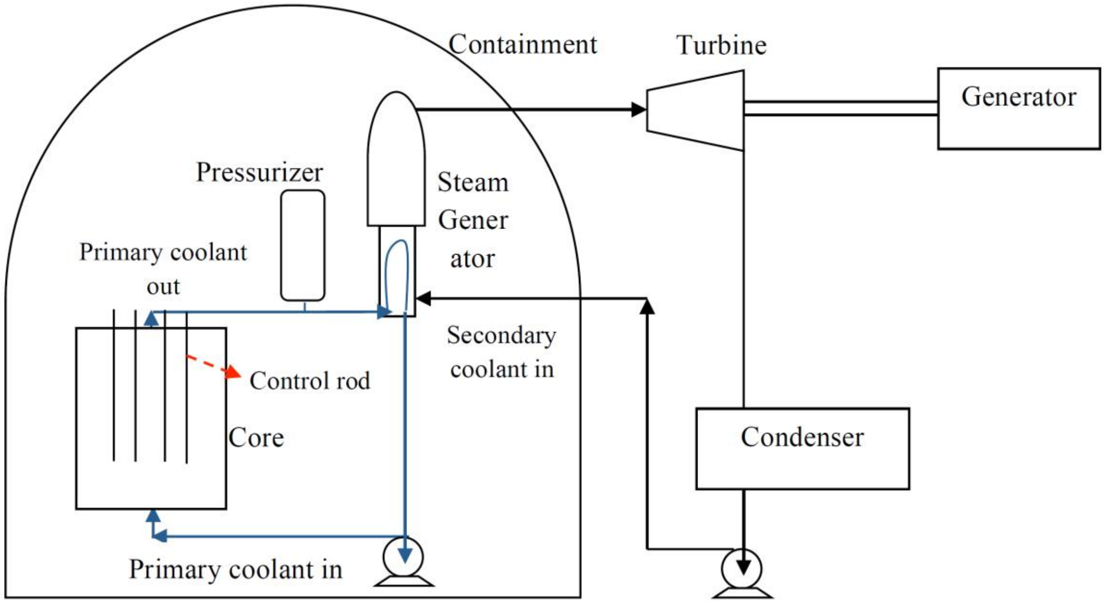


Fig. 31. Schematic diagram of Pressurized Water Reactor

The important components of a **PWR** are (i) A core that contains the fuel (ii) Steam generators (iii) Pressurizer. These components are housed inside the containment (concrete dome that is visible in the plant site). Other components required for power generation like turbine, generator and condenser are located outside the containment.

Two coolant cycles (primary and secondary coolant cycles, with water used as coolant for both cycles) are used in a pressurized water reactor. The primary coolant is circulated through the core in order to remove the heat generated by nuclear fission. The primary coolant maintained at a pressure of **~152 bar**, enters at about **288°C** and leaves at about **324°C** depending upon the core configuration. The high pressure ensures that water remains in liquid state even at high temperatures (boiling point of water at **152 bar** is **343°C**). The pressure in the primary loop is maintained by a pressurizer.

In the steam generator, primary coolant comes into thermal contact with the secondary coolant. Primary coolant passes through large number of tubes in steam generator, while the secondary coolant (inlet temperature **~ 227°C**) occupies the region between the tubes. This facilitates thermal contact between primary and secondary coolants. The pressure in the steam generator **(69 bar)** is lower than the reactor operating pressure. Accordingly secondary coolant (also water) boils at a lower temperature **(285°C)** than that of the primary coolant. Hence, heat transferred from the primary coolant to secondary coolant (flowing in the annular region between the tubes and shell of steam generator) results in the vaporization of secondary coolant. This results in the generation of steam in the steam generator. Steam, thus produced is used to run the turbine for power generation. The spent steam is condensed in a condenser and returned to the steam generator as secondary coolant along with make-up water. The primary coolant, after transferring heat to the secondary coolant, returns to the core to remove the heat generated during nuclear fission. Thus, the Pressurized Water Reactor follows two-coolant cycle or indirect cycle.

The primary coolant loop contains Reactor Pressure Vessel **(RPV)**, Pressurizer, Steam Generator and Coolant pump. Reactor Pressure Vessel **(RPV)** consists of core, water and control rods. The reactor vessel has a cylindrical body with the covers (head and bottom) being hemispherical in shape. The top cover (head) is removable. This permits refueling of the reactor. The reactor vessel is provided with inlet nozzle **(cold leg)** and outlet nozzle (hot leg) for each primary coolant loop. The material of construction of the reactor vessel is manganese molybdenum steel. The parts of reactor vessel in direct contact with coolant are clad with stainless steel. This increases the resistance of material to corrosion. The core is enclosed in a barrel-shaped structure called ‘core barrel’. Fuel assemblies, moderator and coolant are housed in the core. The coolant enters the reactor vessel through the inlet nozzle and impinges on the core barrel. The coolant is directed in the space between reactor vessel and core barrel and reaches the bottom of reactor vessel. The coolant changes its path and moves around and through the fuel assemblies, thereby removing the fission heat. The heated water leaves vessel through outlet nozzle (hot leg) and enters steam generator.

Pressurized Water Reactor Core

Let us look at the details of core of a typical **PWR** designed by Westinghouse Electric Company, USA. Fuel (**UO_2** in this case) is converted to a pellet (8.2 mm diameter and 13.5 mm long) and then clad in tubes of Zircaloy (**98 % Zr**, **1.5 % Sn**, rest other metals). The fuel rod is about **3.7 m** long and **1 cm** in diameter and can accommodate about 271fuel pellets. A small space is provided between the pellets and the fuel rod to account for the expansion of the fuel pellets and to accommodate gaseous fission products like Xenon and Krypton. An array of **17 x 17** fuel rods constitutes a fuel bundle or assembly. Allowing few spaces in the array for control rods, approximately **263** rods comprise an assembly. About such 193 fuel assemblies make up the core, resulting in **50,952** fuel rods and about **13,807,992** fuel pellets. Control material (silver-indium-cadmium alloy) is used in the form of rod. These rods are inserted into the core from the top to control the reactor power. The steps involved in conversion of a fuel pellet to fuel assembly are shown in **Fig. 32**.

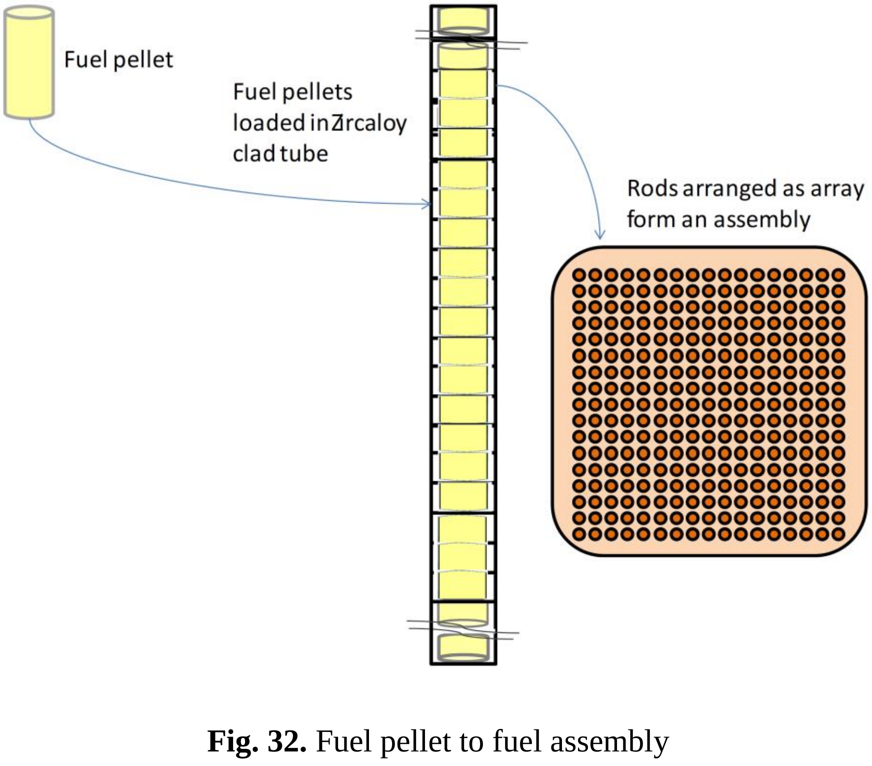


Fig. 32. Fuel pellet to fuel assembly

- **Pressurizer**

Pressurizer is a vertical, cylindrical vessel whose bottom is connected to the reactor coolant system (primary coolant) by a single piping. The pressurizer contains stagnant water and steam. The pressure is regulated by varying the temperature of water. When the pressure in the primary coolant loop decreases, electrical heaters placed in pressurizers are activated, heating the water. As water is heated in closed system both temperature and pressure increase (due to generation of steam). In case of higher pressure in the primary loop, a spray located at the top of the pressurizer is activated resulting in condensation of steam (by water spray) and subsequent reduction in pressure.

A schematic diagram of pressurizer (along with animation) is shown below **(Fig. 33)**:

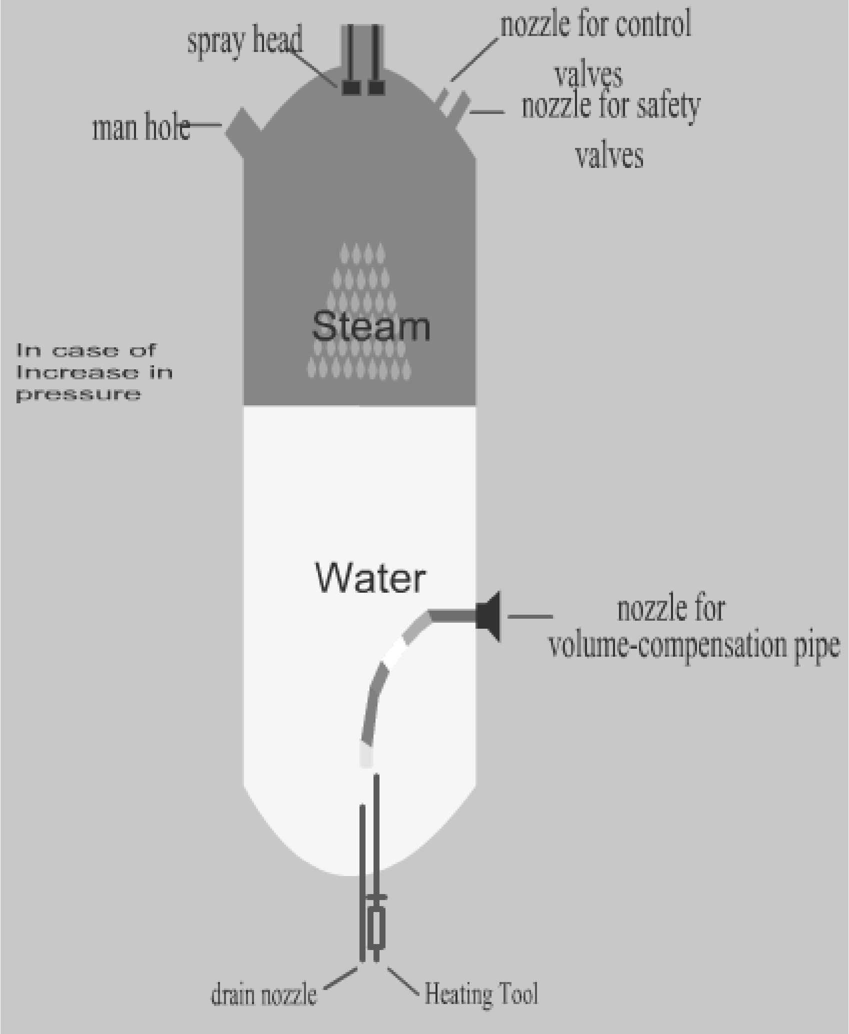


Fig. 33. Schematic diagram of Pressurizer.

Among several support systems for the primary coolant, one of the important systems is Chemical and Volume Control System **(CVCS)**. This system is designed to (i) maintain the purity of primary coolant with the help of filters (ii) maintain the boron concentration at desired levels by addition of boron or by replacing a part of borated water with water (dilution) and (iii) to maintain water level in pressurizer at desired level. For the purpose of maintaining purity of primary coolant, a small amount of water is continuously passed through this system. The details of steam-water circuit comprising steam generators, turbines, condensers and feed water heaters will be discussed in the later modules.

- **Comparison of fuels for nuclear reactors**

The nuclear reactors in operation around the globe utilize uranium (or) plutonium based materials as fuel. The fuel may be in the form of a metal or metal oxide, or metal carbide or metal nitride. Let us look at the important properties of fuel and their implications, which are shown in **Table 1**. These properties serve as the criteria for selection of fuel materials.

Table 1: Important thermo-physical properties of nuclear fuels and their implications

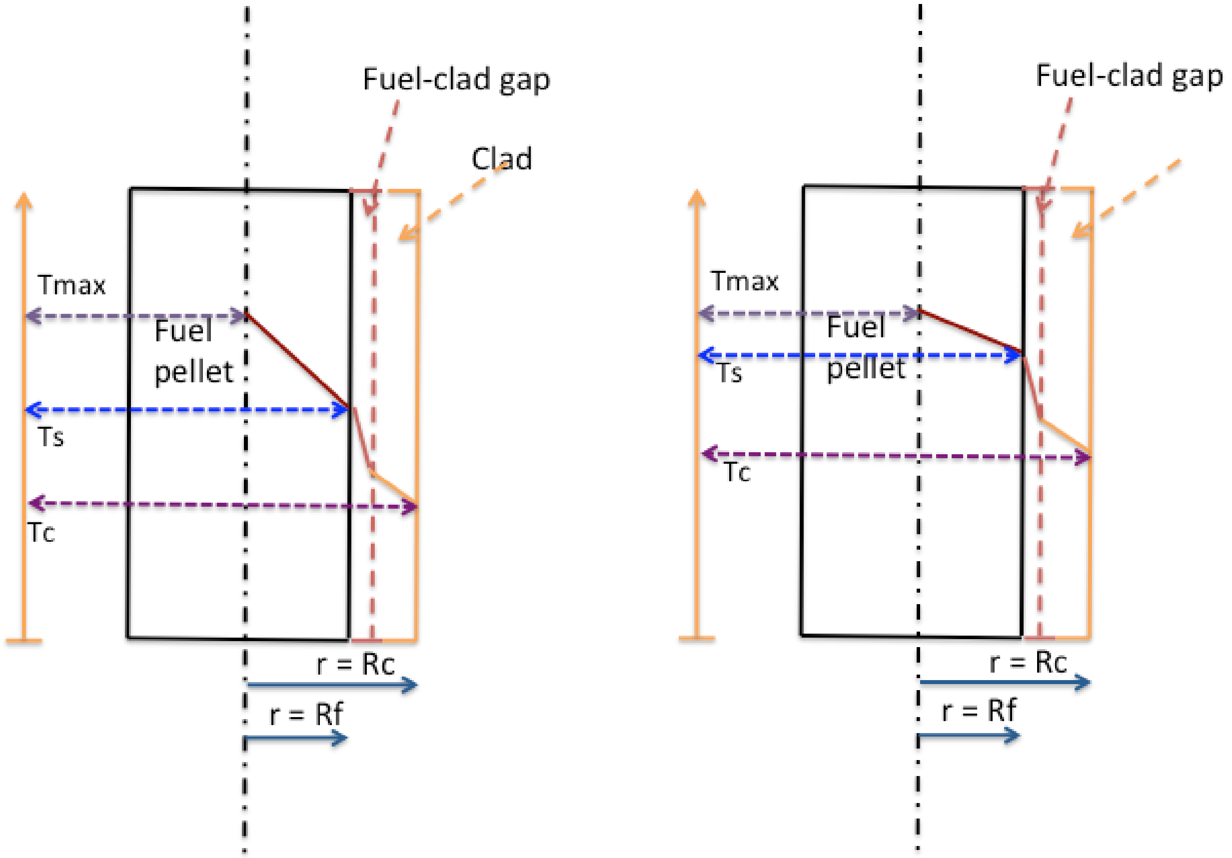
Property	**Implications**
Nuclear properties: Absorption cross section, fission cross section, fission products, neutron production, energy released	Determines the mass of fissile required, volume of the core
Thermal conductivity	Indicates the ability of a material to transfer heat by thermal conduction. Higher values of thermal conductivity are desirable for fuels. This would facilitate rapid removal of heat from the fuel. As a result, with fuel of higher thermal conductivity the temperature gradient in the fuel will be low. In nutshell, higher thermal conductivity fuel permits the reactor operation at high power density and specific power (power per unit mass of fuel) without leading to excessive temperature gradients.
Melting point	Defines the limiting power of a fuel element. Reason: The maximum temperature that a fuel can be allowed to reach is influenced by the melting point. Lower the melting point of the fuel, lower is the maximum permissible temperature and the power of a fuel. Hence, fuels with higher melting points are desired

Dimensional stability	The fuel must exhibit dimensional stability at high temperatures and neutron irradiations. Increased burn up must not result in compromise of dimensional stability. Swelling results in compromise of dimensional stability. Swelling may arise either due to high temperature or neutron irradiation or both. A fuel with higher tendency to swell is likely to constrict the coolant channels. With excessive swelling, fuel may come in contact with cladding resulting in rupture of cladding and release of fission gases. A ceramic fuel like $\mathbf{UO_2}$ retains fission gases more effectively and is less prone to swelling.
Coefficient of thermal expansion	A measure of expansion of a material with increase in temperature. It may be recalled that a small gap exists between the fuel pins and the cladding in the radial direction called fuel-cladding gap. When the fuel and cladding have different coefficients of thermal expansion then one of the following scenario may happen: (i) If the thermal expansion coefficient of fuel is more than that of cladding, the fuel expands more than that of cladding during heating resulting in reduced fuel-cladding gap. Eventually fuel and cladding may come into contact with each other. (ii) If the thermal expansion coefficient of cladding is more than that of fuel, cladding expands more than that of the fuel during heating resulting in increased fuel-cladding gap. The fuel-cladding gap contains (fission) gases that are poor conductors of heat. With increased fuel-cladding gap, the total thermal resistance for heat transfer between fuel and coolant increases. This causes increase in the temperature of the fuel due to reduced heat transfer.
Chemical properties	In case of cladding failure in terms of cracks,

	there will be direct contact between fuel and coolant. Under these circumstances, chemical stability of fuel while in contact with coolant is important.

- **Oxide fuels**

The important examples in the category of oxide fuels are **UO_2 (Uranium dioxide)** or mixed oxide **(UO_2-PuO_2)**. The major disadvantages of oxide fuels are their lower density and lower thermal conductivity. Lower density leads to the requirement of a larger core diameter. One may be aware of the fact that to pack a certain mass of material of lower density, a relatively large volume of space is required. Since the density of oxide is low, their use requires reactors of larger diameter to be fabricated. Lower thermal conductivity leads to poor transfer of heat from the centre of the fuel pin to the edge of the pin and to the cladding. Hence the temperature at the centre of the fuel must be sufficiently high to ensure that the outer surface is sufficiently hot to transfer heat to the coolant. However, the fuel temperature cannot be allowed to increase beyond certain limits. If the maximum allowable temperature of the fuel is Tmax and that of the cladding is **T_{clad}**, the lower thermal conductivity of oxide leads to a large difference between Tmax and **T_{clad}**. Since the maximum allowable temperature of the fuel limits Tmax, limitation exists on **T_{clad}** as well. This puts a limitation on the maximum temperature of primary coolant and hence that of the steam generated. **Fig. 34** shows the comparison of temperature profiles with two different types of fuels: **(a)** lower thermal conductivity fuel and **(b)** higher thermal conductivity fuel. These profiles are shown for a fixed fuel centre-line temperature. The temperature of a fuel is maximum at the centre-line and decreases radially outward in a cylindrical fuel element. A temperature difference exists in the fuel-clad gap due to higher resistance in this gap occupied by fission gases. A small resistance exists in the cladding layer as well. All these result in difference between the maximum temperature of the fuel **(T_{max})** and the cladding surface temperature **(T_c)** with which the coolant is in contact. For a constant heat transfer rate, a higher temperature gradient **(dT/dr)** indicates higher resistance to heat transfer. The gradient may be split up into two parts: **(i)** temperature gradient in the fuel and **(ii)** temperature gradient in fuel-clad gap and in clad material. While comparing two fuels of different thermal conductivities, the temperature gradient in the fuel is more whose thermal conductivity is lower, when compared to that in a fuel of higher thermal conductivity. This is illustrated in the temperature profile shown in **Fig. 34 (a)** and **(b)**. Note that the temperature gradient in fuel-clad gap and in clad is same in both **Fig. 34 (a)** and **(b)**. However, the temperature gradient (shown as sharp decrease in temperature with radial position) in **Fig.34 (a)** is high due to use of low thermal conductivity fuel.



Fuel with low thermal conductivity or high Tmax-Ts

Fuel with high thermal conductivity or low Tmax-Ts

Fig.34. Temperature profiles in **(a)** low thermal conductivity fuel **(b)** higher thermal conductivity fuel. The profiles are drawn for the same fuel centre-line temperature.

The dimensional stability, chemical and irradiation stability, compatibility with clad material and coolant make the metal oxide (uranium oxide) the most widely used fuel in light water reactors. In fast reactors, where the temperature and neutron flux are higher, **UO_2** responds to environment and hence **UO_2-PuO_2** (mixed oxide) fuel is used.

- **Metallic fuel**

It is well known that the thermal conductivities of metals are greater than that of metal oxides. Accordingly, metallic uranium has better thermal conductivity compared to that of **UO_2**. The density of metallic uranium is also higher than that of **UO_2**. However, metallic uranium undergoes a change in crystalline phase at **660°C**. A substantial change in the volume of metal is experienced as a result of this phase change. This results in damage to the integrity of the fuel elements. Owing to this, metallic uranium is not used as fuel in power reactors.

- **Metal carbide and nitride fuel**

Uranium carbide and uranium nitride have higher density and thermal conductivity than uranium dioxide. These fuels are inferior to uranium dioxide as far as the compatibility with cladding, swelling under irradiation and retention of fission gas are concerned. Hence, these were used in test reactors only.

- **Boiling Water Reactor (BWR)**

As the name suggests, these are the reactors where coolant boils in the reactor pressure vessel itself. The boiling water reactor utilizes enriched uranium (with **U-235** content about **3%**) as the fuel and light water as both moderator and coolant. A **BWR** operates at a relatively lower pressure of about **76 bar** in such way that water boils in the core at about **285°C**. Steam-water mixture leaves the core, with water separated from steam in a steam separator. A steam dryer is used to produce dry steam required to run the turbine for power generation. A schematic sketch of a **BWR** plant is shown in **Fig. 35**.

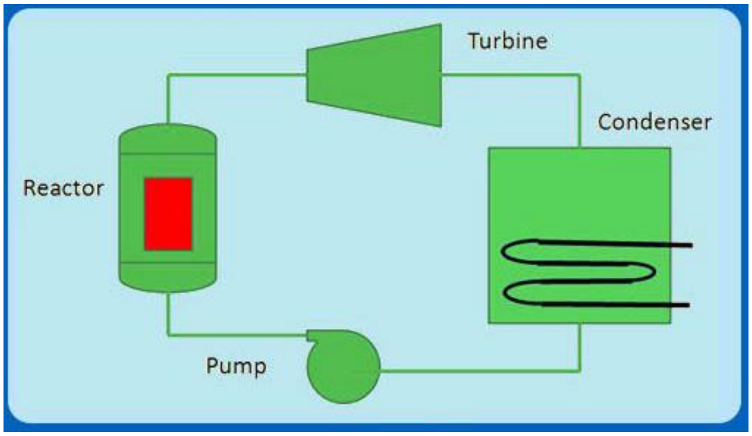


Fig. 35. Boiling Water Reactor **(BWR)-I (BWR)**

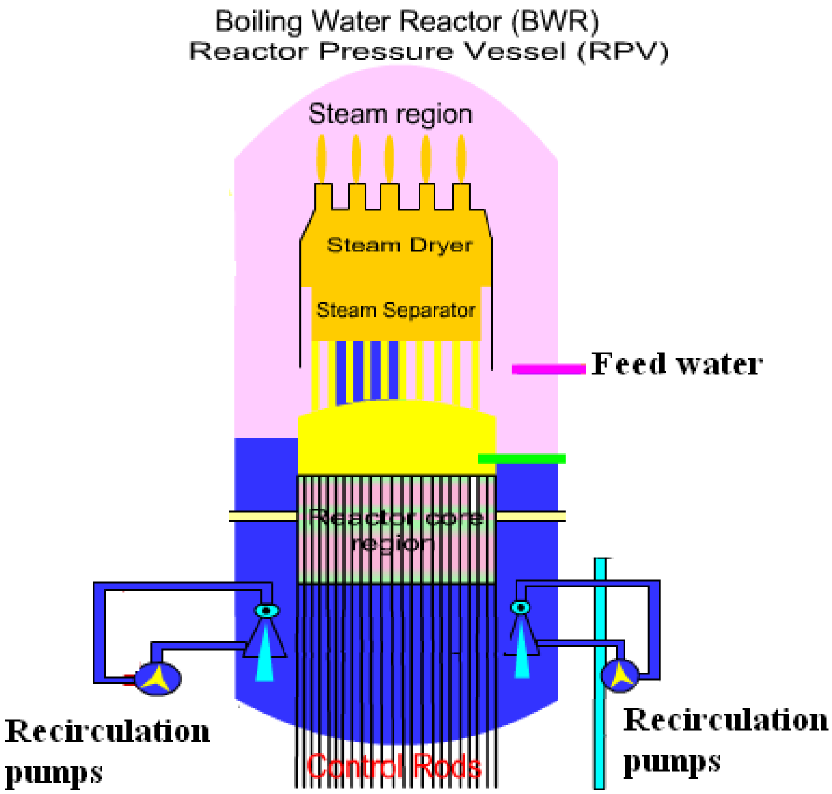


Fig. 36. Reactor Pressure Vessel of BWR

Fig. 36 shows the Reactor Pressure Vessel **(RPV)** of a boiling water reactor. The feed water (coolant) enters through the nozzles located high on the vessel, but below the water level. Hence the feed water mixes with the saturated water returning from the steam separator, resulting in subcooling of saturated water. This mixture flows through the downcomer (annular region between the vessel and steel shielding the core) while a recirculation pump located outside the reactor pressure vessel facilitates the mixing. This mixture, supplied to the bottom of the core through jet pumps, rises up as it gains heat and undergoes a temperature increase. In the top part of the core, about **15 %** (by volume) of the coolant contains steam and hence represents a two-phase mixture (steamwater mixture). Steam separators separate steam-water mixture and returns water to the core. Steam, then passes through a steam dryer, before expanding in a turbine for power generation.

The salient differences between PWR and BWR are

- The operating pressure of **BWR** is lower than that of a **PWR**

- Separate steam generators are not required for **BWR** as the steam is generated in the core itself
- There is only one coolant loop in **BWR** as against two in **PWR**
- There is no requirement for pressurizer in **BWR** as against the requirement of a pressurizer in **PWR**
- Control rods are inserted from the bottom in **BWR** as against their insertion from top in a PWR. The moderating capability of water is higher at lower temperatures. At increased coolant temperatures near the top of the core, appreciable boiling results in the formation of steam, leading to reduced moderation. Hence to control the reactor power, control rods must be inserted from the bottom where the flux of thermal neutrons is high.

BWR plant is a simpler one due to lack of steam generator, pressurizer and the associated pipelines. The lower operating pressure in **BWR** leads to lower structural problems compared to that of a **PWR. BWR** plant has good response to operational transient where in higher temperature results in boiling of water resulting in steam and hence a reduction in moderation and heat generation.

- **BWR Fuel Assembly**

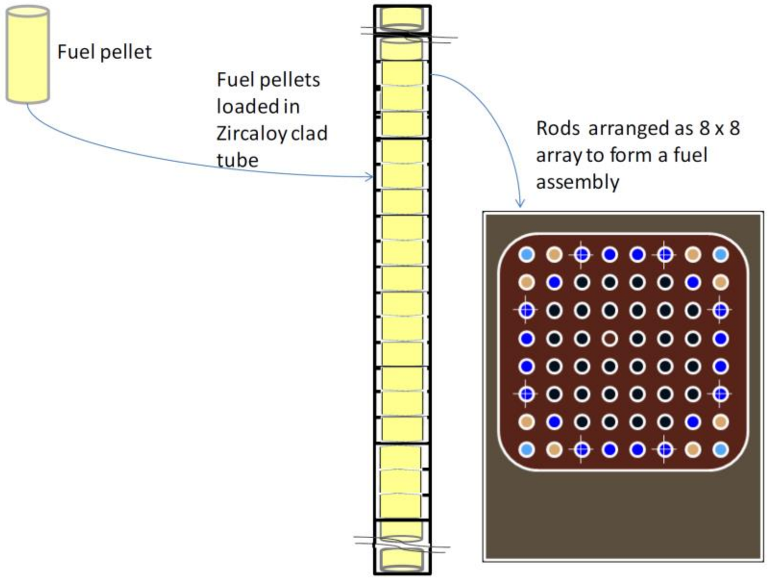


Fig. 37. Preparation of fuel assembly

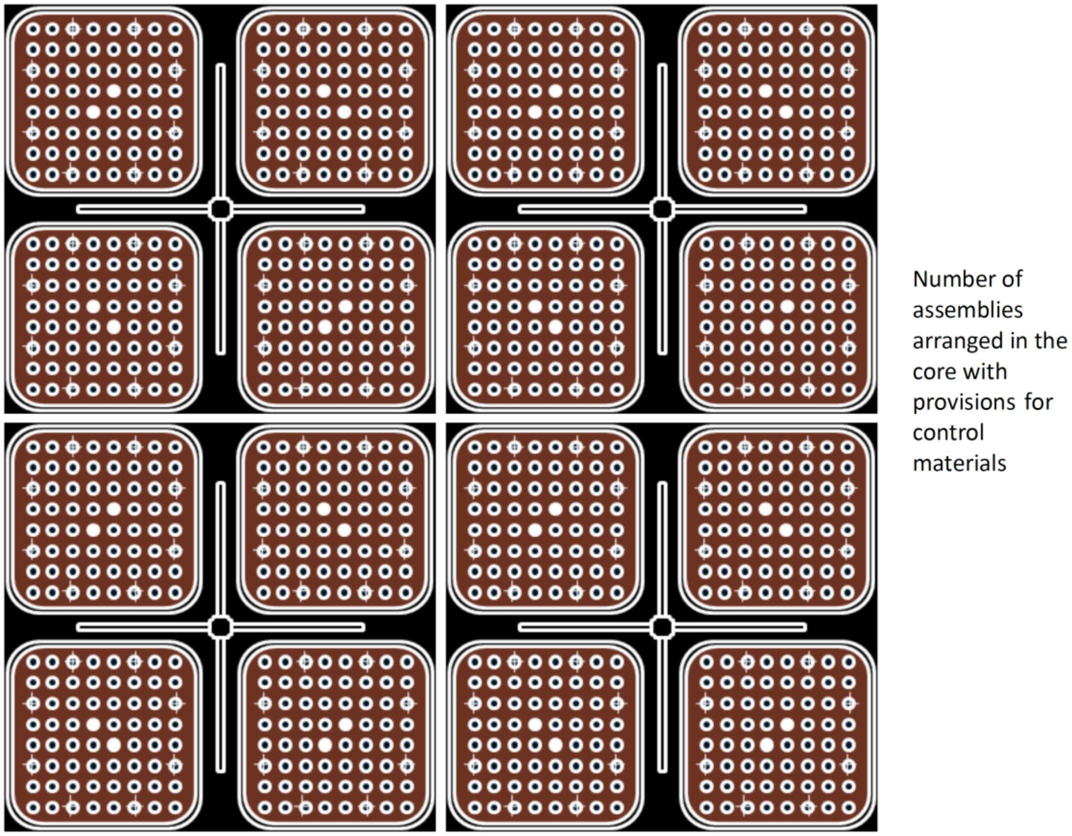


Fig. 38. Arrangement of fuel assemblies in **BWR** core

The preparation of fuel pellets, loading them in cladding rods and arranging them in square arrays are similar to that in a pressurized water reactor. Spacing is provided between fuel assemblies for accommodating control material in the form of plates. **Fig. 37** and **Fig. 38** show the steps in the preparation of fuel assembly and their arrangement in the core respectively.

Boiling water reactors follow single-coolant Rankine cycle. This is a direct cycle, while the power cycle in pressurized water reactors is an indirect cycle. The efficiency of the cycle depends on the temperature of steam and that of cooling water available in the condenser.

Introduction to renewable energy sources

Renewable energy sources derive their energy from existing flows of energy from ongoing natural processes, such as sunshine, wind, flowing water, biological processes, and geothermal heat flows. A general definition of renewable energy sources is that renewable energy is captured from an energy resource that is replaced rapidly by a natural process such as power generated from the sun or from the wind. Currently, the most promising (aka economically most feasible) alternative energy sources include wind power, solar power, and hydroelectric power. Other renewable sources include geothermal and ocean energies, as well as biomass and ethanol as renewable fuels.

❖ Solar

The recent disasters in the southeastern United States highlighted the decline in the world's oil supply, forcing us to begin considering other energy options. One promising technology, solar power is worth considering for its sustainable, renewable and emissions reducing qualities. Modern residential solar power systems use photovoltaic **(PV)** to collect the sun's energy. **"Photo"** means "**produced by light**," and **"voltaic"** is **"electricity produced by a chemical reaction." PV** cells use solar energy to generate a chemical reaction that produces electricity. Each cell contains a semiconductor; most commonly silicon in one of several forms (single-crystalline, multi-crystalline, or thin-layer), with impurities (either boron or phosphorus) diffused throughout, and is covered with a silk screen. Cells are joined together by a circuit and frame into a module. Semiconductors allow the electrons freed from impurities by the sun's rays to move rapidly and into the circuit, generating electricity. Commercial residential **PV** modules range in power output from **10 watts** to **300 watts**, in a direct current. A **PV** module must have an inverter to change the **DC** electricity into alternating current energy in order to be usable by electrical devices and compatible with the electric grid. **PV** modules can also be used en masse to create large-scale power plants.

Using **PV** modules to generate electricity can significantly reduce pollution. The most energy used in creating solar panels is used to purify and crystallize the semiconductor material. No official numbers are available on the exact amount of energy used to create solar panels because there is no industry standard for making the crystals. A number of researchers have done work in attempt to address concerns about energy payback for **PV** systems. Assuming 12% conversion efficiency and **1,700 kWh/m^2** of sunlight per year, the estimates range between **2 and 4** years for rooftop **PV** systems to generate the energy it took to make them. The average United States household uses **830 kWh** of electricity per month.

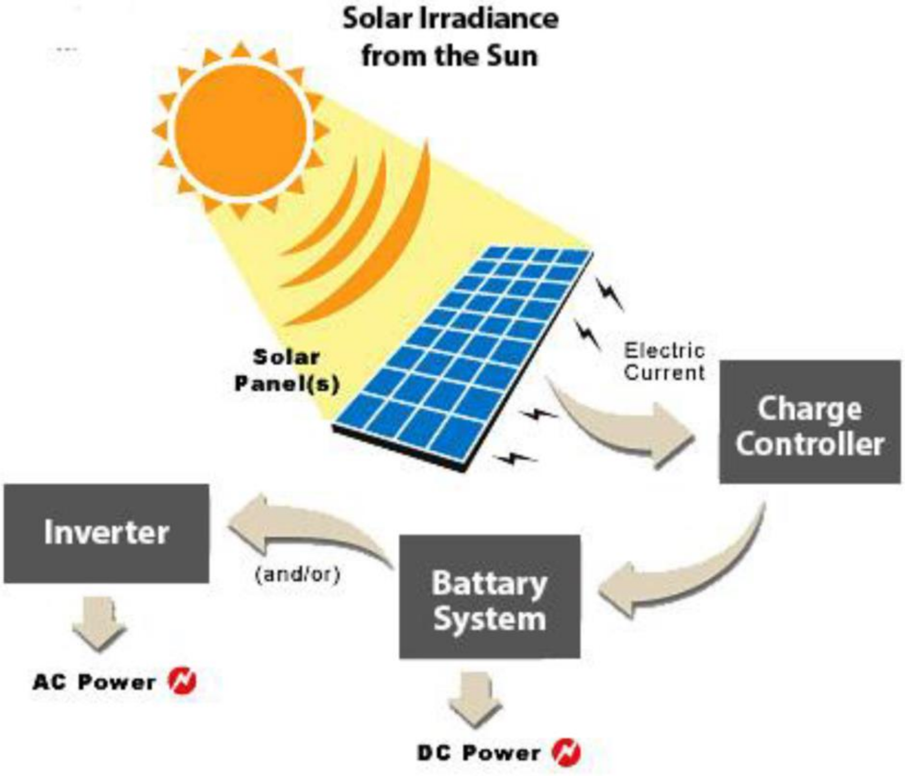


Fig. 39. Generation of **AC** and **DC** power from solar energy

Over twenty years, a **100-megawatt** solar thermal electric power plant can avoid producing over three million tons of carbon dioxide. Estimates regarding pollution prevention suggest that producing **1,000 kWh** of electricity through solar power can reduce emissions by **8 pounds** of sulfur dioxide, **5 pounds** of nitrogen oxide, and **1,400 pounds** of carbon dioxide. Lifetime estimates (over a projected **28 years**) average in the thousands of pounds of prevented emissions. Installing a **PV** system is a hefty investment for homeowners. **5-kW** systems can cost up to **$40,000**. **PV** system power can cost as much as **$9 per watt**, and small systems will not produce enough power to offset electricity costs and save the homeowner any substantial money. As a result, over **30 states** offer incentives (mostly in the form of tax rebates) to help encourage homeowners to purchase and install **PV** systems. California is one of the key states, receiving a huge amount of radiation, with the better part of the industry located there, and high-energy costs. The state of California offers a number of incentives under the Emerging Renewables Program passed by the state legislature. The California Energy Commission offers a rebate of **$4 per watt** to help homeowners affordably install **PV** systems. However, the mortgage financing required to purchase a realistic **PV** system is still quite substantial. As **PV** technology advances, more efficient, easily affordable, standardized, reliable and longer-lasting modules will become available. **PV** systems' value to the energy sector especially in residential capacities, is increasingly apparent. However, the continued high cost means that many homeowners will be deterred from purchasing and installing **PV** systems. The only way to encourage further growth in this sector is for consumers to purchase such systems. The energy emissions reductions are substantial enough to be worth the consideration of the federal government. In order to encourage consumers' interest in **PV** systems and growth in the renewable energy sector at a faster rate, the federal government should create an incentive program to help homeowners and businesses purchase and install **PV** systems, especially on new constructions.

❖ Wind

Wind energy is one of the most promising alternative energy technologies of the future. Throughout recent years, the amount of energy produced by wind-driven turbines has increased exponentially due to significant breakthroughs in turbine technologies, making wind power economically compatible with conventional sources of energy. Wind energy is a clean and renewable source of power. The use of windmills to generate energy has been utilized as early as **5000 B.C.**, but the development of wind energy to produce electricity was sparked by the industrialization. The new windmills, also known as wind turbines, appeared in Denmark as early as **1890**. The popularity of wind energy however has always depended on the price of fossil fuels. For example, after **World War II**, when oil prices were low, there was hardly any interest in wind power. However, when the oil prices increased dramatically in the **1970s**, so did worldwide interest in the development of commercial use of electrical wind turbines. Today, the wind-generated electricity is very close in cost to the power from conventional utility generation in some locations.

- **Where does wind come from?**

Wind is a form of solar energy and is caused by the uneven heating of the atmosphere by the Sun, the irregularities of the Earth's surface, and rotation of the Earth. The amount and speed of wind depends on the Earth's terrain and other factors. The wind turbines use the kinetic energy of the wind and convert that energy into mechanical energy, which in turn can be converted into electricity by means of a generator.

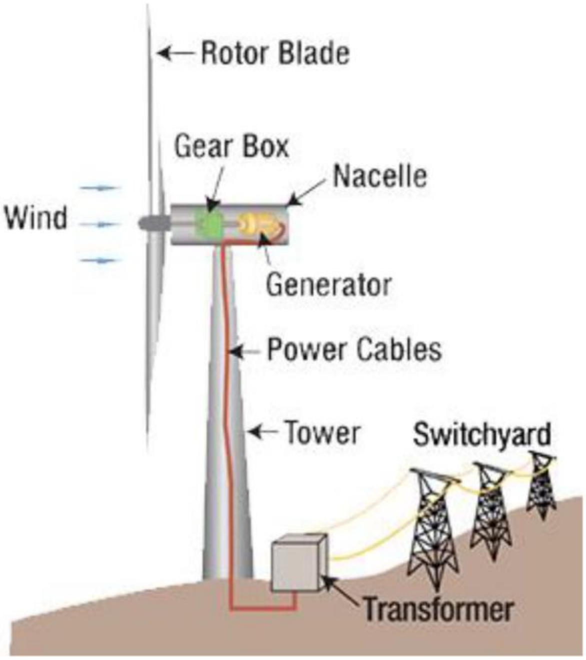


Fig. 40. Horizontal-axis Wind Turbine (**HAWT**)

There are essentially two types of wind turbines: The horizontal-axis variety, and the vertical axis design. The horizontal-axis design is used more commonly and looks like an Old Dutch windmill, whereas the vertical-axis design looks like and eggbeater. These wind turbines generally have either two or three blades, called rotors, which are angled at a pitch to maximize the rotation of the rotors. The horizontal-axis design is slightly more efficient and dependable than the vertical-axis windmill. Most of the windmill models that are currently in production are thus horizontal-axis windmills.

Utility scale turbines can produce anywhere from **50 kilowatts** to several megawatts of energy. These large windmills are generally grouped together in a windy area in what is called a wind farm. The proximity of the windmills in a wind farm makes it easier to feed the produced electricity into the power grid. Wind energy offers many advantages compared to fossil based power and even some other types of alternative energy, which explains why it is the fastest growing energy source in the world. The two main reasons are cleanliness and abundance. The fact that wind is a renewable resource gives it a major advantage over oil and the nonrenewable resources. Considering that environmental pollution is being linked to several global problems that might eventually threaten the existence or at the very least worsen human living conditions, the fact that windmills do not produce any emissions whatsoever is another reason to increase the use of wind turbines. Increasing the percentage of wind power used by the United States would not be unreasonable, seeing that the price of wind power is between 4 and 6 cents. Even though wind energy has many environmental and supply advantages, there are several disadvantages that limit the usability of wind power. The main disadvantage to wind power is that it is unreliable. Wind does not blow at a constant rate, and it does not always blow when energy is needed. Furthermore, the windiest locations are often in remote locations, far away from big cities where the electricity is needed. Just like with any other energy plant, people oppose it because of aesthetic reasons. The rotor noise produced by the rotor blades is another reason for opposition.

Wind seems to be a very good source of alternative energy. Its biggest setback is its unreliability, but in combination with other, more reliable sources, wind energy should be used extensively to supplement the demand for energy.

❖ Hydroelectric Power

Hydropower is America’s leading renewable energy resource. This notable success can be attributed to the fact that out of all the renewable power sources, hydropower the most reliable, efficient, and economical. Furthermore, the concept behind hydroelectric power is fairly simple and has been in use for a significant span of time.

The earliest reference to the use of the energy of falling water is found in the work of the Greek poet Antipater in the 4th century BC. Indeed, the word “hydro” comes from the Greek language meaning “**water**.” Several centuries later, the Romans were the first to utilize the waterwheel. Due to the Romans’ powerful influence on Europe through conquest, the waterwheel was soon commonly found throughout that continent, and by **1800**, tens of thousands of waterwheels had been built. These early waterwheels were of course not used for power generation, but mostly for grinding crops. Water energy was first converted into electricity on **Sept. 30**, **1882** near Appleton, Wisconsin. By **1980** hydroelectric power accounted for about **25%** of global electricity and **5%** of total world energy use, which amounted to approximately **2,044 billion kilowatt hours (kW h).**

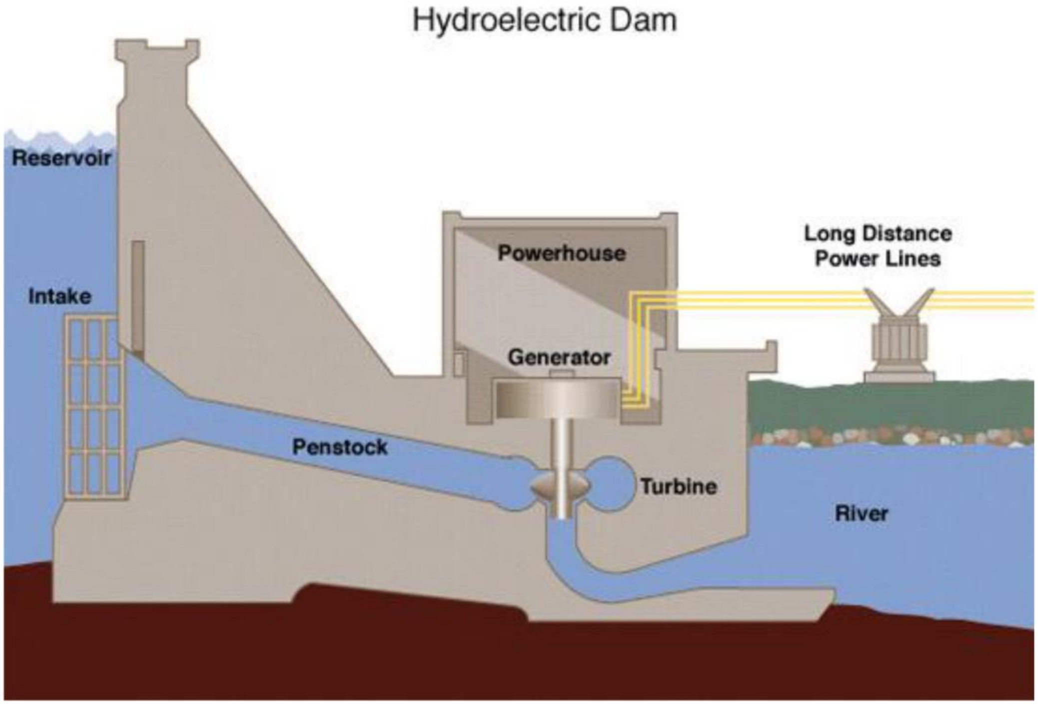


Fig. 41. Hydroelectric Dam

Harvesting energy from water is possible due to the gravitational potential energy stored in water. As water flows from a high potential energy (high ground) to lower potential energy (lower ground), the potential energy difference thereby created can be partially converted into kinetic, and in this case electric, energy through the use of a generator. There are essentially two major designs in use that utilize water to produce electricity: the hydroelectric dam, and the pumped-storage plant. The waterwheel discussed at the beginning of this paper is currently no longer in use and has been replaced by the far more economical and efficient dam. Both the waterwheel and the dam work on the same general principle, but the dam has the advantage of being more reliable due to the reservoir behind it. The principle is simple: the force of the water being released from the reservoir through the penstock of the dam spins the blades of a turbine.

The turbine is connected to the generator that produces electricity. After passing through the turbine, the water reenters the river on the downstream side of the dam. A pumped-storage plant is very similar to the hydroelectric dam, the main difference being that the pumped-storage plant uses two reservoirs, one being considerably higher than the other. The advantage of this design is that during periods of low demand for electricity, such as nights and weekends, energy is stored by reversing the turbines and pumping water from the lower to the upper reservoir. The stored water can later be released to turn the turbines and generate electricity as it flows back into the lower reservoir. Now that the two types of facilities have been discussed, there are also two way of obtaining the water: dam and run-of-the-river. A dam raises the water level of a stream or river to an elevation needed to create the necessary water pressure. In a run-of-the river scenario, the water is diverted from its natural path, enters the turbine, and is later returned to the river. Hydroelectric power offers several significant advantages compared to fossil based power, and even other types of alternative energy. Probably the most important asset of hydroelectric power is its reliability. Furthermore, it creates no pollution, and once the dam is built, even though that process is very expensive, the produced energy is virtually free. A dam has the ability to continuously produce electricity and can adjust to peaks in demand by storing water above the dam and by being able to increase production to full capacity very quickly. Other than the high construction and planning costs, the major drawbacks of large dams are mostly environmental. The dam does not produce harmful emissions as in the case of fossil fuel burning. It does however alter the landscape dramatically, producing several severe, even unbearable changes to the habitat of fish and other plants and animals. Building a large dam will of course flood a large area of land upstream of the dam, causing problems for the animals that used to live there. It furthermore affects the water quantity and quality downstream of the dam which in turn affects plants and animals. Blocking the river also disallows certain migration pattern of fish. Finding sites that are suitable for dams is also a challenge. This is one of the reasons why the hydroelectric power production in the **U.S.** cannot increase by much in the future: most of the suitable locations have already been utilized. According to the Energy Information Administration, the total amount of electricity produced in the **U.S.** through hydroelectric means has increased by **6.3%** from **2004** to **2005**. Even though **U.S.** construction of dams has peaked and is decreasing, advances in turbine technology maintain a slight growth margin of electricity production. Precipitation however also influences the ability of dams to produce electricity. In this sense, **2005** could have been a year of increased precipitation if compared to **2004**. Overall, hydroelectric power seems to be a very good source of alternative energy: one that should be maintained at the maximum level possible. It has the main advantage over all the other forms of alternative energy production in that it is reliable, whereas the other forms of alternative energy are not. The main disadvantage is that hydroelectric energy production in the **U.S.** is currently being used to its maximum potential, which means that large sums of investment will produce only small increases productivity. Other alternative energy sources are not yet as developed and hence will produce greater advances in productivity with the same or even a smaller input of money. Hydroelectric spending should be maintained at current levels, and more money should be invested in the other sources of alternative energy.

❖ Geothermal

Geothermal energy is one of the only renewable energy sources not dependent on the Sun. Instead, it relies on heat produced under the surface of the Earth. Geothermal energy already has several applications and could potentially provide a significant source of renewable power for the United States. However, it is limited by a multitude of factors revolving around the issues of sustainability and economics. There are two main applications of geothermal energy, which include producing electricity at specialized power plants, and direct-heating, which puts to direct use the temperature of water piped under the earth's surface. Geothermal power plants take on several types of forms, depending on the type of geothermal area from which they extract energy. In any case, the plants depend on steam to power turbines and generate electricity, though the methods of producing steam varies depending on the type of geothermal reservoir. Direct-heating, on the other hand, provides immediate, usable energy. This type of energy can heat individual buildings or entire areas, as in the city of Klamath Falls, Oregon. It can also cool buildings by pumping water underground where the temperature remains relatively stable near **60 degrees Fahrenheit**, and then into buildings, where the water absorbs heat, thus helping to air condition the building. The United States also uses direct heating in fish farms, spas, and greenhouses. Geothermal energy could potentially become a major source of renewable power for the United States. This is because geothermal energy reduces the United States dependence on foreign oil, it's extremely reliable due to the constant source of heat emanating from the earth, and it has almost no negative environmental impact. In **2004**, the **US** produced approximately

2300 MW of electricity, and the Department of Energy estimates that the figure could reach **15000 MW** per year within a decade.16 In the grander scheme, however, geothermal energy accounted for only about **0.34%** of total **U.S.** energy consumption, and **5.56%** of renewable energy consumption. But more energy could be extracted using developing technology, which doesn't rely on existing hot water and steam reservoirs. The process involves drilling deep into the surface of the Earth where temperatures are hot, and then injecting water into cracks of rock, which is heated and then pumped back to the surface. If this "hot dry rock" **(HDR)** technology proves effective, then more geothermal plants could operate in more locations, since much of the Earth's surface is underlain by hot, dry rock. Some problems that geothermal energy faces are depletion of both water and heat in geothermal areas. The first problem has been partially addressed by re-injecting water into reservoirs, thus sustaining the plant's ability to operate. However, it has been shown that water re-injection can cause small earthquakes, which raises the question of whether the plants should be liable for the damages caused. In Alameda, California, water reinjection at a geothermal power plant triggered earthquakes of magnitudes up to **3.9** and **3.5** on the Richter scale, which were felt **90 miles** away in the community of Middletown. As of now, there is no government regulation concerning the repayment of damages caused by these earthquakes, though community groups such as the one in Middletown have pressured the plant to compensate homeowners for damages such as cracked chimneys, which can cost about **$10,000** to fix. Heat depletion of geothermal areas is more problematic than water depletion in the long run, since it cannot be avoided. It is caused by a natural cooling-off of the earth's crust, and in these cases, plants would become less and less efficient over several decades until they were rendered useless. Other issues facing geothermal power in the United States are building costs and economic competitiveness with other energy sources. Geothermal plants can be expensive, depending on factors such as how deep the wells must be drilled and the temperature of the water or steam. These initial costs of an economically competitive plant can be as high as **$2800 per kW** installed capacity, which accounts for about two thirds of total costs for the plant. The plants are economically competitive in the long run however, because their fuel is free, whereas natural gas or coal plants spend up to two thirds of their total operating costs on fuel. Another problem that adds cost to geothermal plants is the problem of connecting to energy grids. This is a critical issue because geothermal plants are built where geothermal resources permit- such as geysers and areas with less-heated water. Over time, however, the plants pay for themselves and all the necessary costs because of low operating costs; namely, the fact that the plants energy is free and always available.

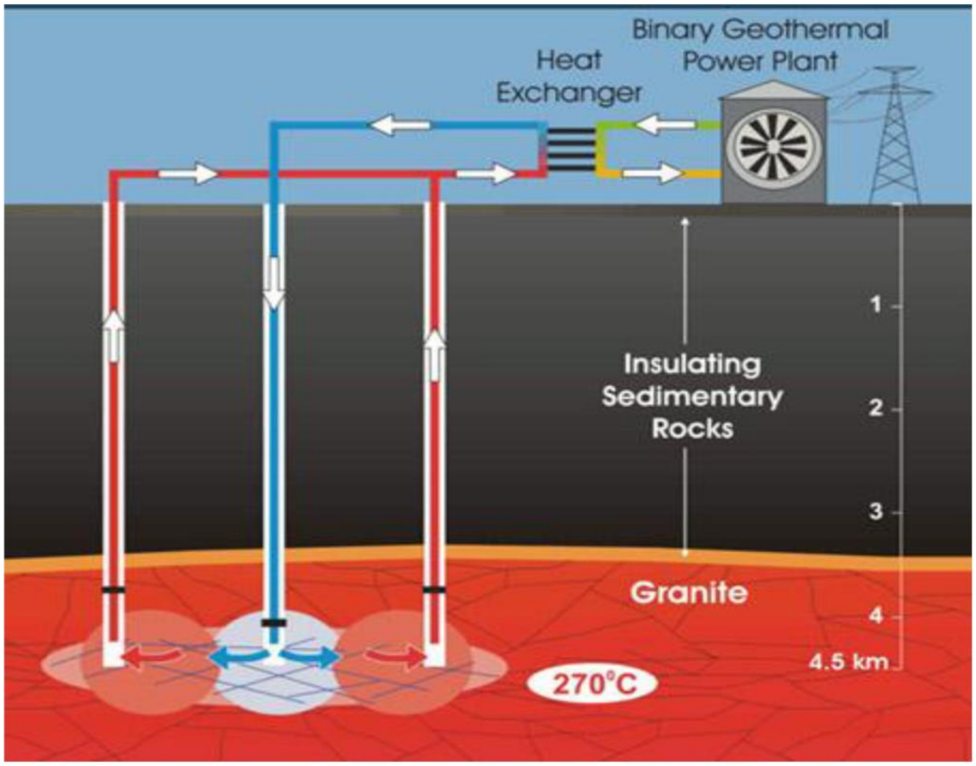


Fig. 42. Binary Geothermal Power Plant

The National Commission on Energy Policy believes geothermal energy can cost from **4-6 cents per kWh**, which depends on the construction of new geothermal plants, but compares favorably with other renewable energies such as solar power, which costs **20-25 cents per kWh**. It's also competitive with coal and natural gas, which costs about **4-5 cents per kWh**. The projected low cost therefore depends on the availability and exploitation of existing geothermal resource Because of its reliability, accessibility, low impact on the environment, and potential low cost, geothermal energy is a very attractive source of renewable energy for the United States. Expanding use of geothermal energy depends largely upon the success of the hot dry rock technology and the simultaneous prevention of earthquakes caused by water injection at those plants and water re-injection at other plants. If the **HDR** technology proves to be viable and safe, geothermal plants can be built in closer proximity to electricity grids, without worrying about geothermal resources like geysers. This would make the plants more cost effective and enable geothermal energy to compete with other energy types.

❖ Biomass

As a pending global energy crisis appears more and more imminent, it is important to consider many different options for new energy sources. Renewable energy sources are ideal because they are more efficient, environmentally friendly and, ultimately, better for consumers. Biomass can be converted into fuels through a number of different processes, including solid fuel combustion, digestion, pyrolysis, and fermentation and catalyzed reactions. Electricity is generated in many places through solid fuel combustion. The majority of America's electricity is fueled by coal combustion. However, many states, especially California, are encouraging companies to use biomass fuels to generate electricity. These products are usually wood matter, vegetation, waste from lumber yards. Power plants burn such fuels to heat a boiler, and the resulting steam powers turbines & generators. This process still releases a lot of carbon dioxide and other polluting gases into the environment, but helps eliminate waste efficiently. Digestion is another process that makes use of existing waste. The term is a misnomer. Digestion is the naturally occurring process of bacteria feeding on decaying matter and making it decompose. It is that which releases gases like methane, hydrogen, carbon monoxide, etc. In many landfills, owners are experimenting with set-ups to best collect the gases produced by such bacteria. The standard system includes pipelines running through the waste to collect the gases. Animal feed lots and other facilities are also exploring tapping such resources. A zoo in upstate New York is using their elephant manure to do the same thing. Benefits of this process include the relative lack of impurities in the gases produced and the fact that the synthesis gases (carbon monoxide and hydrogen) can be converted to any kind of hydrocarbon fuel. A third process, pyrolysis creates a product much like charcoal, with double the energy density of the original biomass, making the fuel highly transportable and more efficient. Anhydrous pyrolysis heats the biomass at intense temperatures in the absence of oxygen or water. Scientists assume that this is the process that originally produced fossil fuels (under different conditions). Most industrial processes of pyrolysis convert the biomass under pressure and at temperatures above **800°F (430°C)**. A liquid fuel can also be produced using this process. The most widely used alternative fuel, ethanol, is created through fermentation of organic materials. Ethanol has a current capacity of 1.8 billion gallons per year, based on starch crops such as corn. Again, the fuel conversion process takes advantage of a natural process. Microorganisms, especially bacteria and yeasts, ferment starchy, sugary biomass products (like corn), yielding products like ethanol, which can be used as fuels in a variety of applications.

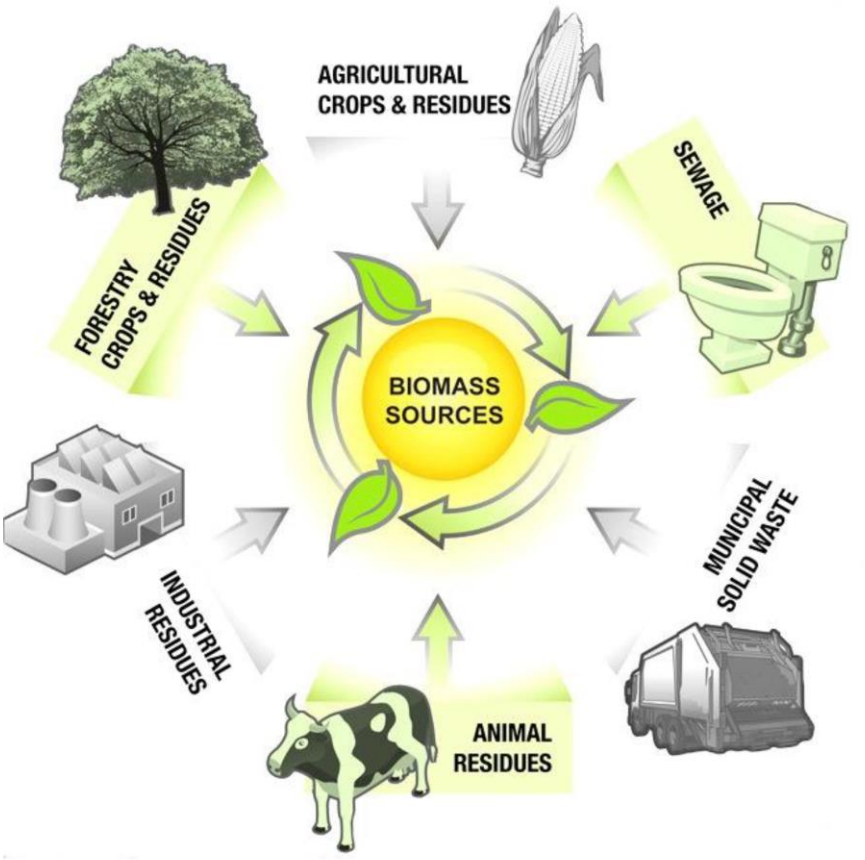


Fig. 43. Biomass Sources

Biodiesel is an increasingly popular fuel, especially in the transportation sector. This monoalkyl ester is formed by combining fuel-grade oil, processed from sources like vegetable oil, animal fats, algae and even used cooking grease, with an alcohol (like methanol or ethanol), using a catalyst. It shows great promise as both a neat fuel (used alone) and as an additive to petroleum diesel. Using biomass could be the answer to the energy questions made more imminent by the recent crises that have further threatened our oil supply. The current technologies take advantage of many natural, long-utilized processes in order to create “new” kinds of fuel. Upon further observation, one realizes that these fuels are very basic, using the most readily available energy sources with very simple, standardized processes that greatly reduce pollution and offer hope for the future.

❖ Ethanol

Fuel-quality ethanol is beneficial for car-owners, the economy and the environment. This growing technology is looking to be an immediate part of the solution to the forthcoming energy crisis. Ethanol, also known as ethyl alcohol or grain alcohol, is a colorless, clear liquid. The chemical formula is $\mathbf{CH_3CH_2OH}$. Fuel-quality ethanol goes through more processes than do alcoholic beverages, in order to make it unfit for human consumption and to increase the purity so as to avoid separation when mixed with gasoline. The most common method for making ethanol used in the United States is the dry-mill method. At the beginning of **2005**, the **81** ethanol plants in **20** states can produce up to **4.4 billion gallons** each year, and the **16 plants** under construction are expected to add **750 million gallons** of capacity. The dry mill process has advanced to the point at which any cellulosic (plant fiber) biomass can be used to make fuel ethanol (and is now being referred to as the Advanced Bioethanol Technology). The variety of feedstock that can be used today includes corn, barley, wheat, cornstalks, rice straw, sugar cane bagasse, pulpwood, switch grass and even municipal solid waste, offering tremendous opportunities for new jobs and economic growth.

Ethanol is not used by itself to fuel cars. Instead, it’s mixed with gasoline. The two most common blends are **E10** and **E85**. The number refers to the percentage of ethanol in the blend. **E10** is a blend of ten percent ethanol and ninety percent gasoline. **E85**, the most mainstream alternative fuel, is eighty-five percent ethanol and fifteen percent gasoline. Using ethanol increases the octane rating and decreases the amount of damaging emissions associated with fuel consumption. It is for this second reason that ethanol use is so strongly recommended and endorsed by state and federal governments. The Clean Air Acts Amendments of **1990** require using **reformulated gasoline (RFG)** to reduce emissions in major metropolitan areas. **RFG** blends gasoline with oxygenates, of which ethanol is increasingly popular. Methyl tertiary-butyl ether **(MTBE)** used to be the most popular, but there are increasing environmental health concerns, regarding seepage, surrounding its use. Oxygenates (compounds with structures similar to that of gasoline, but with the addition of oxygen) dilute the noxious, dangerous gases emitted by gasoline consumption, including nitrogenous oxides, volatile organic compounds and other toxic like carbon monoxide. It is for this reason that the Clean Air Acts Amendments require inclusion of oxygenates like ethanol in the fuel supplies of metropolitan areas, and that the government offers many incentives. These include the Clean Fuel Tax Deduction, taken off the vehicle property tax on new qualified clean fuel vehicles or the conversion of vehicles to run on alternative fuels; the ethanol and biodiesel tax credit, under the American Jobs Creation Act of **2004 (Public Law 108-357)**; the credit for installation of alternative fueling stations, under the Energy Bill of **2005**; the new Flexible Fuel Vehicle labeling requirement, and many more. Approximately one-third of the states offer incentives as well.

Increase in use of ethanol as fuel will benefit farmers economically. The majority of ethanol used today comes from corn, and it is the farmer-owned ethanol plants that are driving the industry's growth. Half of the operating plants are owned by farmers and local investors. The United States Department of Agriculture estimates that the Renewable Fuels Standard would increase the demand for corn for ethanol to **2 billion** bushels each year by **2012**, almost double the current demand, which would raise net farm income to $4 billion. There are drawbacks to using ethanol. The presence of oxygen and smaller molecules means it produces less energy than raw gas, reducing fuel economy by **2 to 3 percent**. The octane boost from ethanol is smaller than that of **MTBE**, and ethanol raises gasoline's volatility, increasing evaporative emissions, all of which are of concern. However, these shortcomings pale in comparison to the health concerns and need to reduce the use of gasoline consumption. There is a reason ethanol blend is required in fuel by Minnesota state law. The environmental and economic benefits make it a desirable alternative. As technology improves, more of the drawbacks will be decreased, and ethanol and other alternative fuels will become mainstream and standard-issue, leading the United States away from our gasoline addiction.

❖ Ocean Energy

Nearly seventy percent of the Earth's surface is covered by oceans, which have the potential to supply humans with an enormous amount of renewable energy. Humans have exploited the vast energy potential of Earth's oceans by taking advantage of wave movement, tides, ocean currents, and ocean thermal energy. The United States, however, has given little or no attention to ocean energy up until this point. This is because of major problems with siting power plants and various economic obstacles. Recent legislation has brightened the future outlook of ocean energy in the United States, but the fledgling technology will take years to realize its potential and account for any significant portion of the United States' consumption of renewable energy

Though the United States does not currently have many power-generating facilities to take advantage of ocean energy, some private and public associations have begun eyeing existing European technologies in hopes of bringing them to American soil or rather, waters. Europe is the world's leader in exploiting ocean energy, due in large part to its location and natural geography. For example, winds blown across the Atlantic from west to east naturally increase the size of waves on Europe's western coast of the west coast of Britain. Larger waves have greater energy, and therefore more power producing ability. Europe has also led the way in technologies that exploit underwater currents and tides. The United States hopes to learn from these technologies, plus the non-European **ocean thermal energy conversion (OTEC)** technology, which is feasible only in equatorial waters like those around Hawaii. The city of San Francisco has recently collaborated with a Scottish group called Scotland's Ocean Power on a demonstration project for capturing wave energy, which is one of the four major types of ocean energy. This technology works on the principle of rolling waves flowing through joints in a large cylindrical pipe, which pushes high pressure oil through hydraulic motors to generate electricity-which is in turn fed to an onshore grid through an underwater cable. Plans are underway to create a "**wave farm**" off the coast of Britain using these wave energy converters. One square kilometer of ocean interspersed with the devices would produce about **30 MW** of electricity, which could power **20,000 homes**. About twenty square kilometers could power the city of Edinburgh. The **U.S.** has similar ambitions in areas of the Pacific Northwest, like Orego, Washington, and southern regions of Alaska. In terms of price, the technology in Europe provides electricity at the equivalent of about **9 cents per kW**, which is about twice the price of wind power in Europe. Obviously then, the technology has a way to go before it becomes competitive in Europe, and especially the United States, which is further behind. There are numerous other variations of wave-energy systems besides the one mentioned, falling into the categories of onshore, near-shore, or offshore systems; but in any case, the systems manipulate wave motions to power hydraulic pumps or spin turbines, thus generating electricity which is fed via cable to the nearest electricity grid. Americans see another example of ocean energy technology in France, which is home to the world's largest **(240 MW)** tidal power plant. Tidal power plants such as the one in La Rance, France, operate by damming an estuary and generating electricity from water flowing through turbines. There are a number of variations in terms of exactly how electricity is produced, but one popular method is called ebb generation. At high tide, water flows in through openings in the barrage, or dam, spinning turbines to generate electricity. The water is retained behind the barrage until low tide, when it flows out again, once again spinning the turbines and generating electricity. The predictability of tides makes tidal power a reliable energy source, though it can only produce electricity at certain times of day: during high and low tides. Unfortunately, there are only a handful of places in the world where tidal power generation is efficient, and the United States is not home to many. These places observe a difference of about **5-10 meters** between high and low tide, which is ideal and also costs for building these types of projects run high, deterring investors who want quicker returns on their money. Tidal power plants typically have negative impacts on estuarine ecosystems as well, adding a further obstacle to their implementation.

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Module-4

Combustion

❖ Fundamentals of thermochemistry:

Thermochemistry describes the thermal behaviour of a reacting system. The transfer of heat energy between a system and its surroundings occurs by the difference of temperature. The transfer of this energy takes place from a hotter body to a colder body until the temperatures of the two bodies become equal or the molecular energies of the two bodies become the same. The change of states also may happen due to this heat transfer. Combustion is a chemical reaction between a fuel and oxygen. The heat energy generates from the combustion of a fuel with air where the internal energy of the fuel species is the chemical energy. This energy is associated with the chemical bonds and intermolecular attractions. During chemical reaction, some chemical bonds are broken with the formation of new compounds with the transfer of some heat energy between system and its surroundings. The heat of reaction is the quantity of heat exchanged between a system and its surroundings during a chemical reaction at a specified temperature. The heat of combustion is defined as the quantity of heat released in combustion of a fuel with oxygen. Some important properties such as, pressure, volume, temperature, internal energy, enthalpy, entropy and free energy are required for quantitative analysis.

The properties, depending only on the final and initial conditions of that system, are called state functions and they are independent of the path connecting with the initial and the final state. The most important state function related with a chemical reaction system is enthalpy. Enthalpy is usually evaluated at standard state, 1 atm pressure and **298 K** of temperature. This property is used to evaluate the heat or energy evolved or absorbed in a reaction. The enthalpy of an element at standard state is assumed to be zero. The absolute value of the enthalpy of a process cannot be determined, rather the enthalpy change of the process can be determined. The enthalpy required to form a molecule from its constituent's elements at standard state is defined as the heat of formation, ΔH_f^0. The standard enthalpy of formation of any substance is defined as the enthalpy of that substance compared to the enthalpies of the elements from which it is formed.

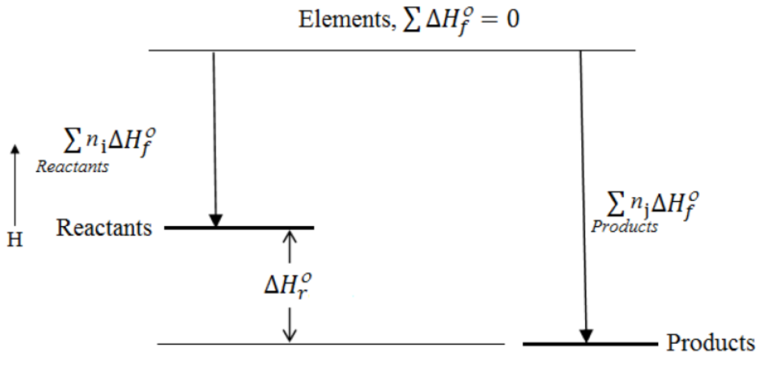


Fig. 44. Heat of reaction from standard heat of formation

Thus, the standard enthalpy change of formation of carbon dioxide by the reaction of carbon and oxygen from their elemental forms is called the standard enthalpy of formation of carbon dioxide or the heat of reaction for combustion $\left(\Delta H_r^0\right)$ The standard heat of formation of each element of a fuel are required for determination of Heat of reaction for the combustion. This can be explained by the diagram as shown in **Fig. 44**.

This can be expressed by the equation

$$\Delta H_r^o = \sum_{products} n_j\, \Delta H_{formation}^o - \sum_{reactants} n_i\, \Delta H_{formation}^o$$

Where, n_i and n_j are the stoichiometric coefficients in the chemical reaction of reactants and products respectively. Thus, the heat of reaction can be derived from the available heats of formation data.

The reaction may be written as,

$$C(graphite) + \; O_2(g) \rightarrow CO_2(g)$$

ΔH_f^0 (i.e. the enthalpy change) at **298 K** is $-393.51\, kJ\, mol^{-1}$. The knowledge of thermochemistry is essential to determine the molar heat of reaction. The amount of heat energy released during reaction will be obtained from the difference of internal energy between products and reactants. The reaction where heat is released by the reaction is called exothermic reaction. The combustion reactions are exothermic reactions. The thermochemical calculation is performed either at constant volume or constant pressure. The reactions are generally carried out at constant pressure.

We have $H = U + PV$ where H is the enthalpy, U is the internal energy and PV is pressure-volume work.

The enthalpy change of a process is given by $\Delta H = \Delta U + P\Delta V$

From first law of thermodynamics, $\Delta U = \Delta Q - w$. In the present system, the work done *(w)* in the system is the pressure volume work. However, because the system remains at a constant volume, the work done $P\Delta V = w$ will be zero. $\Delta Q = \Delta U$

At constant pressure process, assuming ideal gas law $PV = RT$ and $\Delta nV = \Delta V$, we have

$P\Delta V = RT\Delta n$, Δn is the number of mole change in a reaction or,

$$\Delta H = \Delta U + RT\Delta n$$

The heat change at constant pressure process is $\Delta Q = \Delta H$ and, at constant volume is $\Delta Q = \Delta U$. In liquid phase reaction the volume change is also negligible and ΔH is same as ΔU. Let us consider a reaction in a general form $A + B \rightarrow C + D$

The heat change or the enthalpy change of the reaction is equal to the difference in enthalpies of the products and reactants.

$$\Delta H = H_{products} - H_{reactants} = (H_C + H_D) - (H_A - H_B)$$

The change in enthalpy of complete combustion of one mole of a substance for burning in excess air is called the heat of combustion.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -394.5\ kJ/mole$$

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H = -108.8\ kJ/mole$$

Carbon monoxide also may oxidized as

$$CO(g) + \frac{1}{2}O_2 \rightarrow CO_2 \ \Delta H = -283.4 \ kJ/mole$$

The quantity of heat is released depends on the enthalpy of the fuel and oxidant relative to that of the enthalpy of the combustion products. Hydrocarbon fuels on combustion in oxygen produce carbon dioxide and water with the release of heat. The most relevant law for the evaluation of the energy of the reaction system is the Hess' Law. This law states that the total amount of heat evolved or absorbed in a chemical reaction is the same whether the process takes place in one or more steps. This is also known as the law of constant heat summation. In order to explain the Hess' Law, the burning of carbon to carbon dioxide reaction is used. The reaction may take place in two different ways:

1. Direct burning of carbon to carbon dioxide.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5 \ kJ/mole$$

2. Carbon first burnt to CO and CO is further oxidized to CO_2

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H_1 = -110.4 \ kJ/mole$$

$$CO(g) + \frac{1}{2}O_2 \rightarrow CO_2 \qquad \Delta H_2 = -283.2 \ kJ/mole$$

Overall change of enthalpy = $\Delta H_1 + \Delta H_2 = -110.4 - 283.2 = -393.6 \ kJ/mole$.

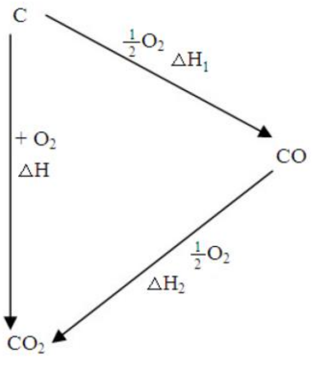


Fig. 45. Application of Hess's Law for the burning of pure carbon.

Hess's law applied for these reactions may be explained in a diagram as shown in **Fig. 45**.

Ex.1: Determine the heat of reaction for $C(s)+2H_2(g)\rightarrow CH_4$ using the following heat of reactions of the following reactions

$$C(s)+\ O_2(g)\rightarrow CO_2(g) \qquad \Delta H_{r,1}=\ -392.5\ kJ/mol \qquad (1)$$

$$H_2(g)+\tfrac{1}{2}O_2(g)\rightarrow H_2O(l) \qquad \Delta H_{r,2}=\ -284.6\ kJ/mol \qquad (2)$$

$$CH_4(g)+\ 2O_2(g)\rightarrow CO_2(g)+2H_2O(l) \qquad \Delta H_{r,2}=\ -885.6\ kJ/mol \qquad (3)$$

Eqn. (2) is multiplied by 2 and added to Eqn. (1),

$$C(s)+\ 2H_2(g)+\ 2O_2(g)\rightarrow CO_2(g)+2\ H_2O(l) \qquad (4)$$

By subtracting Eqn. (3) from Eqn. (4),

$$\Delta H_r=\ -961.7+885.6=-76.1\ \ kJ/mol$$

❖ Combustion air calculation

The reaction of fossil fuels such as, coal or natural gas with oxygen liberates heat and the heat is used for various purposes. The main combustion products of burning of fuels are carbon dioxide and water. Combustion is the reaction of a fuel substance with air or pure oxygen to form combustion products. The combustion process is always exothermic and it liberates heat. The combustion reaction may be written as:

$$Fuel+\ O_2\rightarrow Products+Heat$$

In solid fuel, carbon is the main combustible component which is combined with an equivalent amount of oxygen to form carbon dioxide. Carbon monoxide may also be formed for incomplete combustion, which is further reacted to form carbon dioxide. The hydrogen and sulphur converts to H_2O vapour and sulphur dioxide respectively.

The various reactions observed in the combustion of coal are as follows:

$$C+O_2=CO_2 \qquad (1)$$

$$C+\frac{1}{2}O_2=CO \qquad (2)$$

$$CO + \frac{1}{2}O_2 = CO_2 \qquad (3)$$

$$H_2 + \frac{1}{2}O_2 = H_2O \qquad (4)$$

$$S + O_2 = SO_2 \qquad (5)$$

A definite amount of oxygen is required for the conversion of carbon to carbon dioxide. As per the stoichiometry of Eq. (1), 32 kg of oxygen combines with 12 kg carbon in the first reaction to form 44 kg of carbon dioxide. So, 1 kg of carbon requires 2.667 kg of oxygen. Similarly, 1 kg of carbon requires 1.33 kg of oxygen to form 28 kg of carbon monoxide. 1 kg of sulphur requires 1 kg of O_2. The theoretical air can be calculated for a particular coal if carbon, hydrogen, nitrogen, oxygen and sulfur contents in weight percent are known by ultimate analysis.

❖ Calculation of theoretical combustion air

Calculation on weight basis:

Let the ultimate analysis of a coal sample is as follows:

Carbon: 73%; hydrogen: 4.5%; oxygen 5.9%; nitrogen: 1.5%; sulphur: 5% ; water 2.1%; ash 8%

Oxygen required for burning of carbon, hydrogen and sulphur are as follows:

Basis: 1 kg coal burned

C: 0.73 × 2.667 kg = 1.9469 kg of oxygen

H: (0.045 × 8) - 0.059 = 0.301 kg of oxygen

(1 kg of hydrogen consumes 8 kg of oxygen and 0.059 kg of oxygen is initially present in coal which should be subtracted from the total required oxygen)

S: 0.05×1 kg = 0.05 kg of oxygen

Total oxygen required to accomplish the complete burning = 1.9469+0.301+0.05 = 2.298 kg

One kg of oxygen equivalents to 4.762× 29/32=4.3155 kg ~ 4.32 kg of air, because, molecular wt of air and oxygen are 29 and 32 respectively. Therefore, total amount air needed for the burning of above coal sample will be 2.298 × 4.32 = 9.927 kg, which is the theoretical air requirement.

Therefore, oxygen or theoretical air may be approximately determined by the general equations as,

Oxygen required per kg coal = 2.667 C + (H×8- O) + S kg

Air required per kg carbon = 4.32× (C × 2.667 + (H×8- O) + S)

= 11.521 C + 34.56 H + 4.32(S-O) kg

Where C, H, O and S are weight on the basis of 1 kg fuel and the oxygen present in the fuel is subtracted from the required oxygen for burning of fuel as shown in the equation.

Calculation on volume basis:

The volume of air requirements may also be determined in Nm3 per kg of fuel. 1 kmol is equivalent to 22.4 Nm^3.

1 kg of oxygen is equivalent to (1/32) kmol = (1/32) $\times$ 22.4 = 0.7 Nm^3

So, 1 kg carbon required 32/12 kg oxygen = (32/12) $\times$ (1/32) $\times$ 22.4 = 1.886 Nm^3

Volume of oxygen required = $(1.866C + 5.56H + 0.7S - 0.7O)$ Nm^3/kg

As the volume ratio of air: oxygen is 1: 0.21.

Therefore, the volume of air = Volume of oxygen /0.21

= $(1/0.21)\ (1.866C + 5.56H + 0.7S - 0.7O)$ Nm^3/kg coal

= $8.89\ (C + 0.375S) + 26.5H - 3.3O$ Nm^3/kg coal

A common example of burning of gaseous fuel is the combustion of natural gas which mainly contains methane. One molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water vapor.

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad (6)$$

❖ Excess air calculation

In a combustion process, the complete burning cannot be accomplished with the exact theoretical amount of air. Therefore it is essential to supply an excess amount of air for the combustion of fuel. The volume of twice the theoretical air may be used; otherwise, it is decided based on the nature of the fuel used and the method of burning process. The valid reason for incomplete combustion of fuel in presence of theoretical amount of air may be due to the fact that each particle of oxygen in the air does not have the intimate contact with the fuel particles in the combustion process. Therefore an excess air is to be supplied. It was observed that 50 per cent more than the theoretical amount of air is usually needed. If less than this amount of air is supplied, the carbon burns to monoxide instead of dioxide.

An excess of air is also a source of waste, as the products of combustion will be diluted and carry off an excessive amount of heat in the chimney gases, or the excess air will so lower the temperature of the furnace gases as to delay the combustion to an extent that will cause carbon monoxide to pass off unburned from the furnace.

❖ Calculation flue gas volume of combustion of methane

Stoichiometric equation is $CH_4 + 2O_2 = CO_2 + 2H_2O$ with pure oxygen

$CH_4 + 2O_2 + 7.524N_2 = CO_2 + 2H_2O + 7.524N_2$ (2 mole oxygen= 7.524 moles of nitrogen, that means, 7.524+2=9.524 moles of air)

1 mole of methane requires 9.524 moles of stoichiometric air or 9.524 ml of air at STP per ml of methane.

Flue gas composition:

Ex.: In combustion of pure methane gas with 5% of excess air, determine the gas composition of flue gas in volume %.

Solution:

Basis: 1 mole of methane burning If 5% excess air is used, according to the following equation, oxygen in air is, 2+ 2×0.05=2.1 moles and nitrogen in air is, 7.7524+7.524×0.05=7.9 moles.

$$CH_4 + 2.1O_2 + 7.9N_2 = CO_2 + 2H_2O + 7.9N_2 + 0.1O_2$$

Total number of moles in flue gas = 1 mole CO_2 + 2 moles H_2O + 7.9 mole N_2 + 0.1 mole O_2 = 11 moles

Composition in volume percent is CO_2=0.0909; H_2O = 0.182; N_2= 0.718; O2 = 0.00909 According to the *wet* (water is liquid) analysis.

Ex: Methane is burned with 18 % excess air in respect of volume. Determine the carbon dioxide percentage in the flue gas dry basis.

Solution: The reaction is $CH_4 + 2O_2 = CO_2 + 2H_2O$

$1m^3 \quad 2m^3 \quad 1m^3 \quad 2m^3$

Basis: 1 m^3 methane burning

The volume of stoichiometric air = 2/21 × 100 = 9.524 m^3

The volume of actual air = 9.524 (1+0.18) m^3= 11.238 m^3

Volume of Nitrogen = 11.238 m^3 × 0.79 = 8.878 m^3

Volume of Carbon dioxide = $1m^3$

Volume of Oxygen = $2m^3$ × 0.18 = 0.36 m^3, Total volume of flue gas = 10.238 m^3

% of Carbon Dioxide = 1/10.238 × 100 = 9.767

- ***Stoichiometric ratio***

If the minimum air is used following the stoichiometry of the combustion reaction then the air is called the stoichiometric air. The ratio of actual air to stoichiometric air is called stoichiometric ratio. For example, soichiometric air for burning of methane is

$$Stoichiometric \quad ratio = \frac{Actual\ air}{Stiochiometric\ air}$$

$$Excess\ air = \frac{Actual\ air - Stoichiometric\ air}{Stoichiometric\ air}$$

$$Excess\ air = (Stoichiometric \quad ratio - 1) \times 100\ \%$$

Ex: Calculate the percentage excess air for methane burning. The flow rate of methane and air are 25 and 290m^3/h respectively.

Stoichiometric air for methane burning is 9.524 m^3 /m^3

Assuming the flow rate of methane = 25 m^3/h

The flow rate of air = 290 m^3/h

Air required = 25 × 9.524 =238.1 m^3/h

Then Stoichiometric ratio $= \frac{290}{238.1} = 1.22$

Excess air = (1.22 – 1) × 100 % = 22 %

❖ Calculation of calorific value of fuels

The heating value or calorific value of a combustible material is an important property, which may be used to evaluate its effectiveness for using as a fuel and also for the design of chemical equipment where it is to be used. The calorific value may be defined as the quantity of heat liberated by the complete burning of a unit mass of the fuel with oxygen at constant volume process. In case of gaseous fuel, the heat released during the complete combustion of one cubic meter of gas at **N.T.P (normal temperature and pressure)** i.e., 1 atm pressure at 0°C is the measure of calorific value. Whereas, the calorific value for solid fuel is measured per gram or per kg of solid fuel.

In general, the calorific value of a solid or liquid fuel is the gross calorific, which is determined at constant volume for a liquid fuel and for gaseous fuels at constant pressure. If the water formed and liberated during combustion is in the liquid phase, then the corresponding calorific value is called gross calorific value. The net calorific value corresponds to the process when the water formed during combustion remains as steam.

The calorific value of fuel depends on the type of exothermic reaction and the heat of reaction. Heat of combustion is measured from the heat of reaction of the reaction. It is determined from the value of enthalpy change for the reaction at constant pressure and temperature. At constant pressure system, the enthalpy change is obtained from the equation.

$$\Delta H = \Delta U + RT\Delta n \qquad (1)$$

Therefore, the enthalpy change for the reaction may be determined from the internal energy and number of mole changes in the reaction. The internal energy change with the change of temperature is given as

$$\left(\frac{dU}{dT}\right)_P = C_V \ or \ \left(\frac{d\Delta U}{dT}\right)_P = \mathit{\Delta} C_V$$

$$\mathit{\Delta} U_2 - \mathit{\Delta} U_1 = \int_{T_1}^{T_2} \mathit{\Delta} C_V dT = \mathit{\Delta} C_V (T_2 - T_1) \qquad (2)$$

From the knowledge of thermodynamics, $\left(\frac{dH}{dT}\right)_P = C_P$

and $\left(\frac{d(\mathit{\Delta} H)}{dT}\right)_P = \mathit{\Delta} C_P = C_{P,2} - C_{P,1}$ (3)

$$\mathit{\Delta} H_2 - \mathit{\Delta} H_1 = \int_{T_1}^{T_2} \mathit{\Delta} C_P dT = \mathit{\Delta} C_P (T_2 - T_1) \qquad (4)$$

The heat of reactions may be determined from Eq. (2) and (4), where the subscripts ‘1’ and ‘2’ are designated as reactants and products. T_1 and T_2 are the average temperature of reactants and products respectively. C_P and C_V are the heat capacities at constant pressure and constant volume respectively. The use of average heat capacities in the above equation is a well approximation. The heat of reaction may be determined from the heat capacities of all reactants and products. The heat capacity is usually the temperature dependent extensive property in thermodynamics. It may be expressed as

$$C_P = A + BT + CT^2 + DT^3$$

The values of the constants *A*, *B*, *C*, *D* etc. are available in the literature. The calorific value of solid or liquid fuel may be measured by the bomb calorimeter.

From the summation of all heat of reactions of the possible reactions in the burning process of a fuel may give an idea of the heating value or the calorific value of the fuel. This procedure is easily applicable for the gaseous fuels. For gaseous fuels, such as, natural gas, LPG and producer gas, the heat of combustion is sufficient to be used as an approximate calorific value for natural gas.

The composition of the fuel gas should be known. Then the values for the heat of reaction for oxidation of each constituent to CO_2 and H_2O at 25^0 C are to be determined. The heat of reaction also can be determined from the standard heat of formation data of products and reactants. The summation of all these heat of reactions are made to obtain the heat of combustion in kcal or kJ per mole of the gas and further it may be converted in per unit mass or volume. The values of the standard heat of formation ($\Delta H°_f$) of reactants and products are available in the literature.

The water formed during combustion may be either in liquid phase and vapor state, an addition amount of heat is required to vaporize the water present in the fuel. Then the heat generated by combustion, known as the gross calorific value if water is in liquid state after condensing the vapor. Otherwise, the water will be in the vapor state. Then the heating value is called the net calorific value. This is called the net calorific value is obtained by subtracting the latent heat of vaporization (ΔH_v) from the gross calorific value.

- ***Example: Calculating the heating value of Methane***

It may be assumed the methane is burnt in pure oxygen and does not contain any water vapor.

The reaction stoichiometry is $CH_4(g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O(g)$

The ΔH_{comb} of methane at 298K is the heat of reaction between CH_4 and O_2 to form CO_2 (g) and H_2O (g). The heat of formation data are as follows:

$\Delta H°_f$ of CO_2 (g)= –393.5 kJ/mol, $\Delta H°_f$ of H_2O(g) = –242.8 kJ/mol and

$\Delta H°_f$ of CH_4(g) = 74.8 kJ/mol

Then the heat of combustion of methane is calculated from the equation

$$\Delta H_r^0 = \sum_{products} \Delta H_{f,j}^0 - \sum_{reactants} \Delta H_{f,i}^0$$

$$\Delta H_r^0 = -393.5 + 2(-242.8) + 74.8 = -804.3 \text{ kJ/mol}$$

So, the heat of combustion of methane at 298 K is 804.3 kJ/mol assuming water formed is in vapor phase, this is same as the net calorific value of methane. If water is in the liquid phase, then the heat ΔH_f^0 of H_2O liquid $= -286.2\ kJ/mol$.

$$\Delta H_r^0 = -393.5 + 2(-286.2) + 74.8 = -891.1 \text{ kJ/mol}$$

The heating value or heat of combustion is 891.1 kJ/mol, which 86.8 kJ/mol more than the value obtained for water in vapor phase. The heat of vaporization of water = 86.8/2=43.1 kJ/mol. This heating value is identical to gross calorific value.

The calorific value for gaseous fuel may be experimentally determined using Junker's gas calorimeter. The calorimeter consists of a combustion cylinder surrounded by a water jacket and fuel burner is kept below the combustion cylinder. The flow of cooling water may be adjusted by a control valve. The temperature of the gas exhaust, cooling water inlet and outlet temperatures are measured. The burner is set in such a way so that a complete combustion of the gaseous fuel is occurred. The flow rate of water is then measured. Temperature of the exhaust gas is brought down to the ambient temperature by the flow of cooling water. Water vapour contained in the flue gas is condensed. The heat released by the combustion process is used to heat up the gases inside the combustion chamber (i.e. air and fuel). Then the gases are cooled by the cooling water and the outlet water temperature is increased. If the flue gas is cooled down to ambient temperature, then the heat of the hot gas is completely transferred to the cooling water. Assuming the continuous water flow rate, a steady state heat balance may be written as:

$$m_F H_F + m_W . C_W . (T_{wo} - T_{wi}) = Q$$

If the heat loss from the calorimeter body to surrounding is negligible for the temperature of wall of the instrument is same as the ambient temperature. So, $Q = 0$.

$$Gross\ Calorific\ Value, H_F = [m_W C_W . (T_{wo} - T_{wi})]/m_F\ .$$

Where, m_F and m_W are the mass flow rate of fuel and water respectively. T_{wo} and T_{wi} are outlet and inlet temperature of water respectively. C_W is the specific heat of water.

If water is condensed and collected from the gas outlet for a specified time interval, then the net calorific value is $H_{F,net} = H_{F,gross} - W_C h_C$ where, W_C = mass of water condensed, and h_C = heat of condensation of water vapor.

The calorific value of solid or liquid fuel may be experimentally determined in a bomb calorimeter. The sketch of a bomb calorimeter is given in **Fig. 2**. The total quantity of heat generated by combustion including the heat needed to vaporize the water is obtained, which is called gross calorific value. These measurements are obtained by burning a representative sample in a high pressure oxygen atmosphere within a stainless steel pressure vessel or bomb. The heat released by this combustion is absorbed by water within the calorimeter and the resulting temperature change of water is noted.

The heat absorbed by the water in the calorimeter, $Q_V = \frac{(m_W + W)C_W(T_2 - T_1)}{m_F}$

Where, W = water equivalent of the calorimeter, m_W = mass of water in the calorimeter, C_W = specific heat of water, m_F = mass of fuel, T_1 = initial temperature of water and T_2 = final temperature of the water.

❖ Adiabatic flame temperature calculation

The temperature of the products in an adiabatic combustion of fuel without applying any shaft work, is defined as the “Adiabatic Flame Temperature”. In a combustion process the heat produced during the exothermic chemical reaction is released to their product and the temperature of the products is raised. There is no possibility for dissipation of the heat to the surrounding and the process will be adiabatic as there is no heat loss to the surrounding. As a result, the temperature of the products suddenly increases and it produces a flame. This will heat up the product gases in flame region and the temperature rise will be maximum. This highest temperature is known as the adiabatic flame temperature. The temperature rise depends on the amount of excess air used or the air-fuel ratio. The flame temperature has the highest value for using pure oxygen gas and it decreases by using air. So, the exact stoichiometric air is to be supplied for better result. With too large amount of excess air the flame temperature will be reduced. When the heat loses to the environment or diluted by the inert gases and there is an incomplete combustion. So, the temperature of the products will be less. The flame temperature is determined from the energy balance of the reaction at equilibrium. There are two type of adiabatic flame temperature: constant pressure adiabatic flame temperature and constant volume adiabatic flame temperature.

- ***Constant pressure adiabatic flame temperature***

From the first law of thermodynamics at constant pressure process

$$\Delta U = Q_p - w_p = Q_p - p\Delta V$$

$H = U + pV$

At constant pressure, $\Delta H = \Delta U + p\Delta V + V\Delta P = \Delta U + p\Delta V$

Under adiabatic condition, $Q_p = 0, \Delta H = 0,$

For equilibrium reaction,

$H_{reactants} = H_{products}$

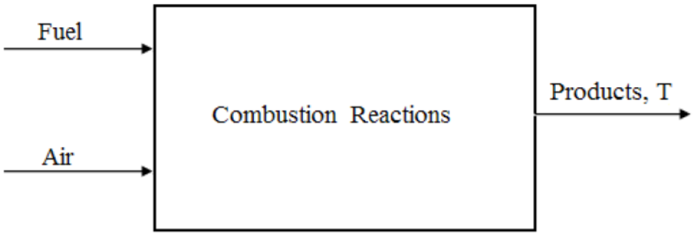


Fig. 46. Combustion of fuel

$$\sum H_{reactants}\,(T_i, p) = \sum H_{products}\,(T, p)$$

$$\sum H_{products}\,(T_i, p) = \sum n_i \int_{T_R}^{T} C_{p_i}\, dT + Q_{VL}$$

Where, Q_{VL} = latent heat of vaporization or condensation for phase change of the product during the change of temperature of from T_R to T K. Ti is the inlet temperature of fuel and air and T_R is the reference temperature, 298 K. Where, C_{pi} is the heat capacities which is expressed as

$C_{p_i} = A_i + B_i T + C_i T^2$

Therefore,

$$\sum H_{products}\,(T_i, p) = \sum n_i[\Delta H^0_{f,i} + A_i\,(T - T_R) + \frac{B_i}{2}(T - T_R)^2 + \frac{C_i}{3}(T - T_R)^2]$$

The flame temperature, T may be calculated from the above equations. It is assumed that $Q_{VL} = 0$ Also if the mean heat capacity data is used,

$$\sum H_{products}\,(T_i, p) = \sum n_i\,[\Delta H^0_{f,i} + \overline{C_{p,i}}(T_{ad} - T_{Ref})]$$

- ***Constant volume adiabatic flame temperature:***

From the first law of thermodynamics,

$Q_V = \Delta U$, and $Q_V = Q_P - nRT = \Delta H_P - \Delta nRT$

In adiabatic process, $Q_V = 0 = \Delta H_P - nRT$

$$H_{reactants}(T_i, p_i) - H_{products}(T_{ad}, p_f) - R(n_{reactants}T_i - n_{products}T_{ad}) = 0$$

Combustion Furnaces

- ***Classification of Furnaces***

Furnaces are used for different thermal processes where heat is produced and transmitted to the solid or liquid material for their processing. The device consists of a furnace with a naturally aspirating gas burner. The produced heat in the furnace may be applied directly to the body of mass to be processed or externally to a separate place. Industrial furnaces are classified according to their uses in various processes such as, smelting, roasting, petroleum refineries different chemical process industries. In general they may be broadly classified as combustion furnace or electric furnaces. The combustion furnaces may be of different types depending upon the kind of combustion, it can be broadly classified as oil fired, coal fired or gas fired. Various furnaces are made with tube bundles inside it and the combustion gases produced in a separate chamber by burning of liquid or gaseous fuels are passed through the tubes. The furnaces may be batch or continuous type according to the requirements.

- ***Gas Combustion Furnaces***

In a conventional gas-combustion furnace, air is forced to flow through the gas burners. The fuel gases are allowed to flow through the furnace. Natural gas is used as the fuel where the combustion products are carbon dioxide, water vapor and other compounds. The combustion gases pass through the furnace where they give up heat across a heat exchanger and are vented out through chimney. A circulating fan passes cooled house air from the return ducts over the furnace heat exchanger, where the air is warmed up and passed into the ductwork that distributes the heated air around the house. An example of gas combustion furnace is the reheating furnace for steel plants

- ***The Reheating Furnace***

The reheating furnace operated in a gas heating system is shown in **Fig. 47**. In this furnace the steel blocks are heated at a desired temperature to bring them in plastic state so that the blocks can be rolled to the desired shape. The temperature usually varies in the range of 900 - 1250^{0}C. The furnace consists of a properly insulated heating chamber made of refractory bricks. This is used for continuous reheating of the stocks.

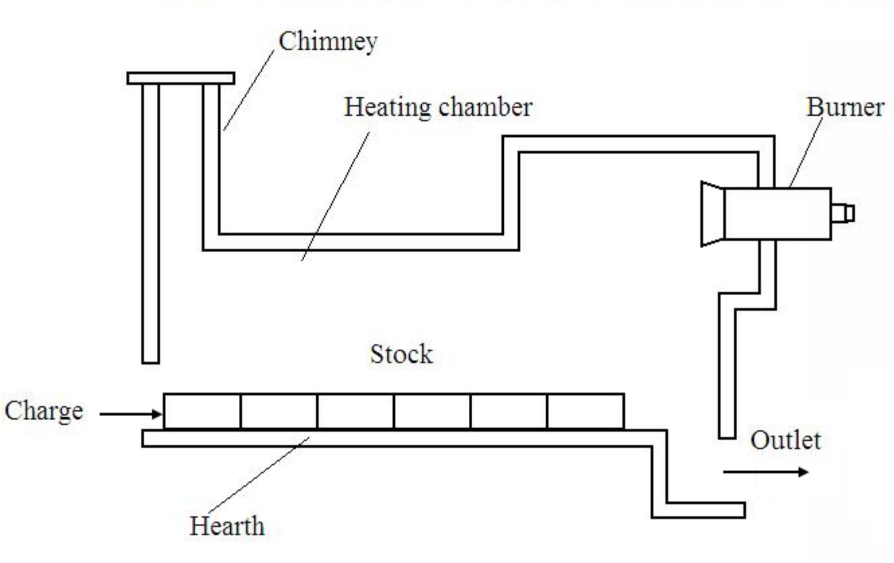


Fig. 47. Gas combustion furnace

The steel stocks enter at one end and exit from the other end. Gas burners are fitted in the furnace. The chimney is provided for removing the combustion gases from the chamber.

- ***The Cupola Furnace***

The coke fired cupola is used in iron foundries for the manufacture of cast iron with a feed of scrap iron or pig iron since ancient times. The cupola furnace has several unique characteristics which are responsible for its widespread use as a melting unit for cast iron. Cupolas is used to melt pig iron or scrap iron with coke and flux. The construction of a conventional cupola consists of a vertical steel shell which is lined with a refractory brick. The charge is introduced into the furnace through a side door situated at middle. The internal diameter of cupolas varies from 450 to 2100 mm with a melting rate of 1 to 30 tons per hour. The use of any cheaper iron scrap as raw feed is an advantage of the process. Where coke is expensive, the gas fired cupola are used. However, the cost of gaseous fuel must be cheaper than coke. The coke-less cupola is very similar to a conventional coke fired cupola. It is an echo friendly process and it was developed since 2003. Instead of coke, light diesel oil or liquefied petroleum gas is used. The natural gas fired cupola is shown with a schematic diagram in **Fig. 48**.

Raw materials are charged on the bed of ceramic beads. Ceramic bed is supported on water cooled grate. The fuel is burnt in air in the burners provided at the bottom of the furnace. Slag is withdrawn by suction process. The furnace is initially heated after the arranging ceramic bed on the water-cooled grate. Then the furnace is charged with the iron raw materials with slag forming substances. Natural gas and air mixture is burned in the burners. Hot flue gas is used to heat and melt the materials. The use of a gas instead of coke drastically reduces the slag formation. The hot exhaust gas transfers the heat to air in a heat exchanger.

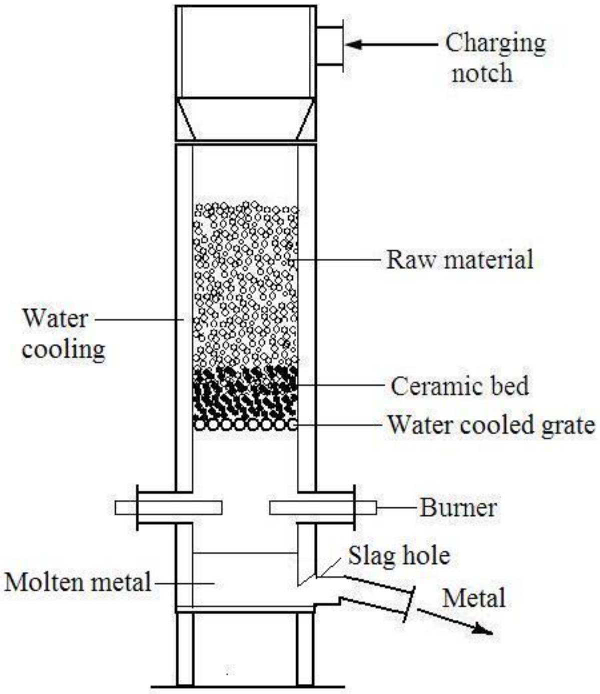


Fig. 48.Natural gas fired cupola

The molten iron and slug comes out at the bottom. The slag is separated from metal by siphon and suction arrangement.

- ***Blast Furnace***

Blast furnaces are vertical tall steel vessel lined with refractory brick. It is major unit of a steel plant which is used for smelting iron ore to form molten pig iron. The approximate height of the furnace and diameter are 90 and 20 ft respectively. The mixture of iron ore, limestone and coke is charged into furnace through the hopper situated at the top. The coke in the charge serves as fuel as well as a reducing agent. The pre heated air at 950 K from the stoves is distributed through the opening at the bottom of the shaft. These openings are called tuyeres (a tube, nozzle or pipe for blowing air into a furnace). The residence time of the charge materials is about 8 hrs. The bottom product is the slag and molten iron. This liquid product accumulates in a vessel which is drained from the furnace intermittently though the outlet. The flue gas from the top of the furnace is cleaned by separating particulate matter from it. Then the energy of the gas is used to preheat the air. Blast furnace is usually operated continuously for 4-10 years.

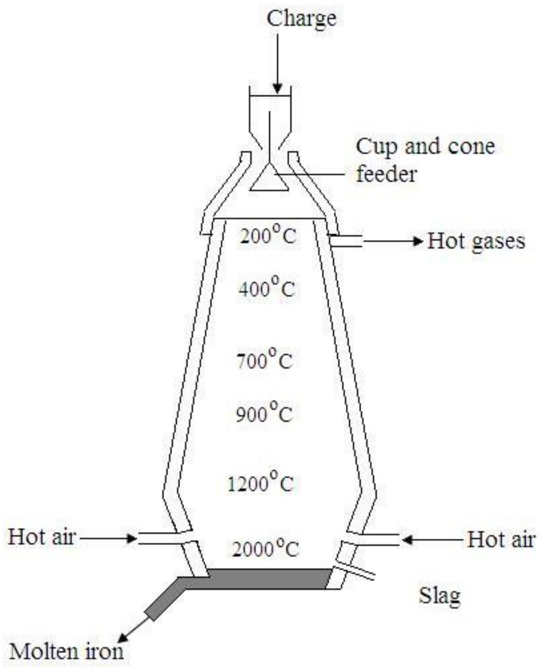


Fig. 49. Blast Furnace

Low iron containing ore are purified to increase the iron content. The coal is converted to coke by carbonization by removing volatile matter in a coke oven plant. The coke is cooled and screened into pieces ranging from one inch to four inches. Limestone forms the slag containing the sulfur compounds. Slag formation starts at 1100^{0}C onwards.

The reactions occuring in a blast furnace are as follows:

1. $3\,Fe_2O_3 + CO \rightarrow CO_2 + 2Fe_3O_4$ at 400-600 ^{0} C
2. $Fe_3O_4 + CO \rightarrow CO2 + 3FeO$ at 600-800 ^{0} C
3. $CO \rightarrow C + CO_2$ at 540-650 ^{0} C
4. $FeO + CO \rightarrow Fe + CO2$ at 800-1100 ^{0} C
5. $CaCO_3 \rightarrow CaO + CO_2$ at 900 ^{0} C

Reductions of metal oxides at 1200-2000^{0}C

6. $FeO + C \rightarrow Fe + CO$
7. $SiO_2 + 2C \rightarrow Si + 2CO$
8. $MnO + C \rightarrow Mn + CO$
9. $P_2O_5 + 5C \rightarrow 2P + 5CO$
10. $S + CaO + C \rightarrow CaS + CO$
11. $CO_2 + C \rightarrow 2CO$

The slag formed mainly contains the four oxides, CaO, MgO, SiO_2 and Al_2O_3 which remain in molten condition at 1200 to 1400^0 C.

Internal Combustion Engine

- ***Historical background***

In the internal combustion(IC) engine, the gases produced from the combustion of gaseous or liquid fuels at high pressure are expanded in a piston cylinder arrangement which helps to transmit the mechanical energy to the crankshaft. Therefore, this device is used to convert thermal energy to mechanical energy. In 1860, J. J. E. Lenoir developed the commercial IC engine where coal gas- air mixture was used as a fuel. The four stroke engine first developed by N. A. Otto in 1867 and the two stroke commercial engine first introduced in 1881 by D. Clerk. Thereafter, Rudolf Diesel invented a different form of internal combustion engine in 1892. Continuous efforts have been given by the researchers for the improvements of the IC engines.

- ***Classification of Internal Combustion Engine***

The engines are classified as the two strokes engine and four strokes engine by the operating principles. The process of ignition and mixing of air and fuel are carried out in two different ways in Otto and Diesel's engines.

In Otto engine, air and fuel are premixed together in the approximate ratio of 15:1 in the carburetor and then introduced into the cylinder for compression. In this engine petrol or gas can be used. Then the mixture is ignited by an electric spark plug and the flame front progresses across the combustion chamber. So it's another name is Spark Ignition Engine (SI-engine).

In Diesel engine, pure air is compressed first and the fuel is injected in the form of droplets at the front of the compressed air. Then the temperature of air increases with the heat of compression and the ignition starts. It is also called as Compression Ignition Engine (CI-engine) . Air fuel ratio varies from 20:1 to 100:1. In this engine diesel oil is used as a fuel.

- ***Four Stroke Engine***

The four strokes of engines are as follows:

1. First stroke: the intake of fuel-air mixture.

2. Second stroke: the compression stroke followed by ignition

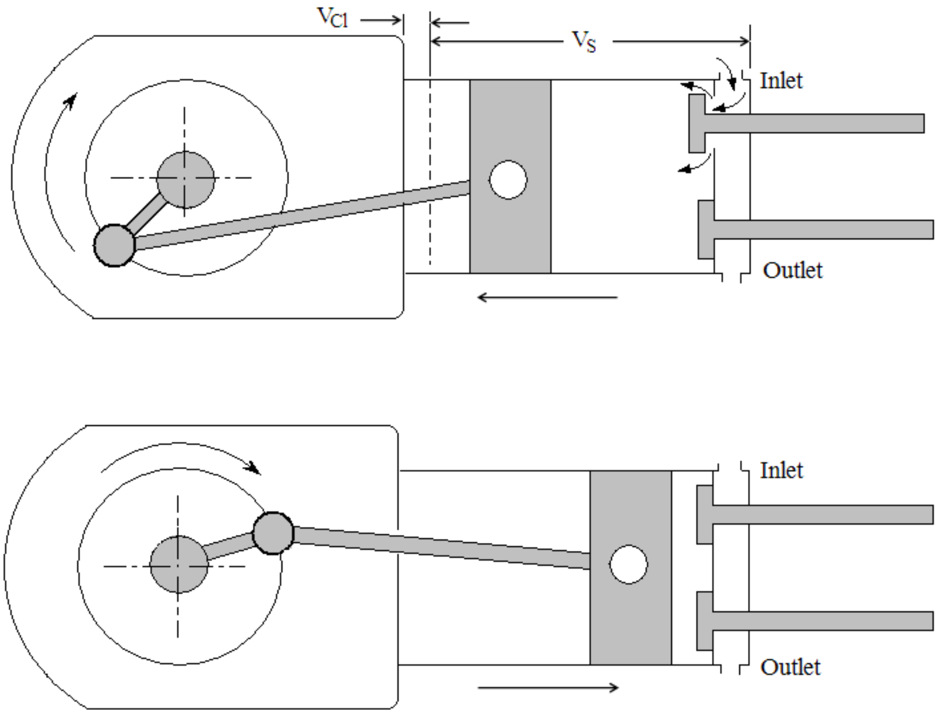
3. Third stroke: the expansion of the combustion gases are work is delivered to the crankshaft

4. Fourth stroke: The exhaust of the flue gases.

- ***Operation of Four Strokes Engine***

The four stroke engine operates on a reciprocating motion of the piston in a cylinder. By the to and fro motion of the piston in a cylinder, the power is transmitted to the crankshaft as shown in **Fig. 50**. The minimum cylinder volume is called the clearance volume $\left(V_{Cl}\right)$ when the piston is closed to the valves end. The volume swept out by the piston is called the swept volume (V_S). Where, $V_S = V_{tot} - V_{Cl}$ and V_{tot} = total volume of the cylinder.

In the first stroke of the engine, the inlet valve opens and oil-air mixture enters the cylinder. This stroke continues from the valve end to the other end. When the piston moves the full length of the cylinder, the inlet valve closes. Then the mixture is compressed by the reverse movement of the piston, which is the second stroke. The oil is ignited at this high pressure by applying a spark when the piston reaches near the end of the cylinder which is called the ***top dead center*** **(TDC)**. Then the combustion starts and the gases are expanded in the cylinder. Then both the valves are closed and both the pressure and temperature of the gases increase. In the third stroke of the piston, the gases expand and the piston moves. The crankshaft starts to rotate and at the end of expansion, the pressure decreases. The outlet valve opens to exit the gases from the cylinder and then the outlet valve closes. In the last stage, the rest of the flue gas escapes from the cylinder and the outlet valve closes. Now the inlet valve opens and the cycle continues by the intake of the fresh air-fuel mixture. All strokes of the pistons are described in **Fig. 50.**



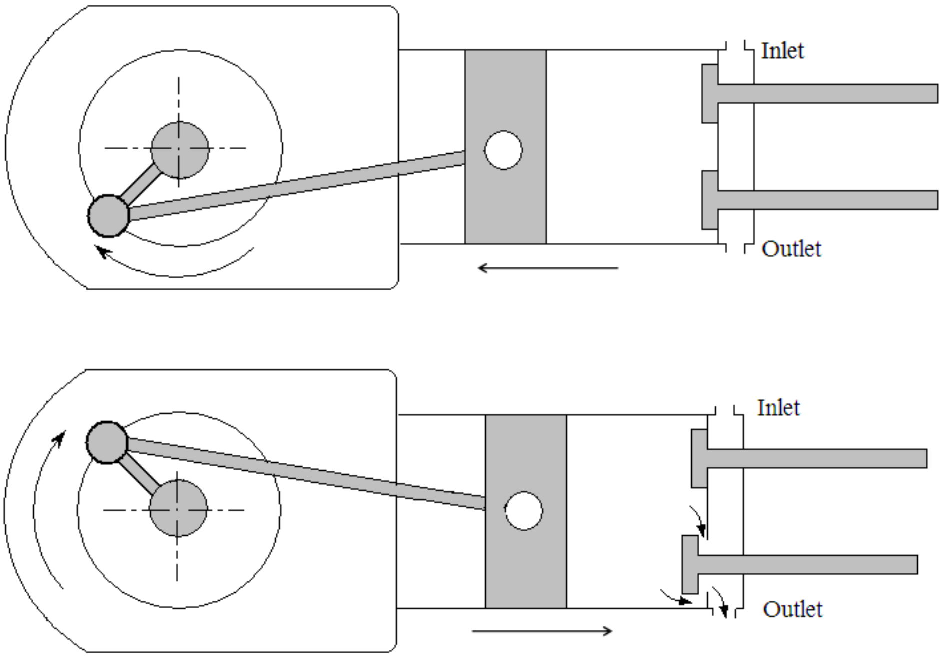


Fig. 50. Operation of four stroke engine

❖ Ideal Engine Cycles

- ***Otto Cycle***

The Otto cycle consists of a four internally reversible processes by which the operation of a petrol engine can be analyzed. The cycle is represented in both the P-V and T-S diagrams. The cycle starts at Top Dead Centre (TDC) and ends at the Bottom Dead Centre (BDC). The distance travelled by the piston from TDC to BDC is called a stroke. The clearance volume (V_{Cl}) is measured after the TDC .The four stroke engine in Otto cycle may be represented as follows:

1. The compression from state 1 to state 2 in a constant entropy process.

2. The constant volume (Isochoric) process from 2 to 3, where the heat (Q_h) is added to the system and the gas-fuel mixture is ignited. Both the pressure and temperature increases.

3. The reversible and adiabatic (isentropic) expansion process occurs from 3 to 4. Work is done on the piston by the expansion of gas mixtures. Both the pressure and temperature decrease.

4. The process 4 to 1 is constant volume cooling, i.e. the heat (Q_c) is removed from the gases.

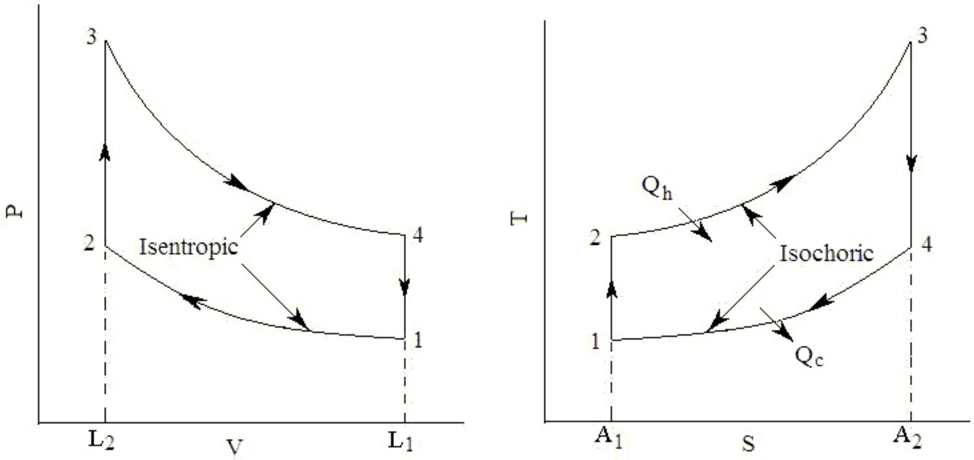


Fig. 51. Otto cycle on P-V and T-S diagrams

Considering unit mass of oil-air mixture, the heat and work relation can be explained by the above two diagrams.

Heat transfer to the gas mixture (heating) per unit mass =

$$Q_h = \int_2^3 Tds = area\ of\ \ 23A_2A_1\,2$$

Heat transfer by the gas mixture to surrounding (cooling) per unit mass =

$$Q_c = \int_4^1 Tds = area\ of\ 41A_1A_2 4$$

The net heat added to the cycle per unit mass = Q_h-Q_c

Similarly from p-V diagram, it may be observed that the work done to the fuel-air mixture per unit mass = $\int_1^2 PdV = Area\ of\ \ 12\,L_2\ L_1\,1$

And work delivers by the engine per unit mass = $\int_3^4 PdV = Area\ of\ \ 34\,L_1\ L_2\,3$

The net work done by the engine = area enclosed by the curves in P-V diagram.

In an isentropic process $\Delta S = 0 = C_V ln\frac{T_2}{T_1} + RTln\frac{V_2}{V_1}$ (1)

It is an adiabatic and reversible process.

For ideal gas assuming C_P and C_V are constant, then $C_P - C_V = R$ and $\frac{C_P}{C_V} = k$

We have, $C_V = \frac{R}{k - 1}$ From Eq. (1) $\frac{R}{k-1} ln \frac{T_2}{T_1} = -Rln \frac{V_2}{V_1}$

$$\left(\frac{T_2}{T_1}\right)^{\frac{R}{k-1}} = \left(\frac{V_1}{V_2}\right)^{R}$$

$$\text{Or, } \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{k-1} \qquad (2)$$

The efficiency in this cycle is given by

$$\eta = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

$$\eta = 1 - \left(\frac{V_1}{V_2}\right)^{1-k} \quad \text{also, } \frac{V_1}{V_2} = compression\ ratio = \eta$$

- ***Diesel Cycle***

Diesel cycle is an ideal cycle by which the working principle of a diesel engine can be represented. In this cycle, air is first compressed to a high pressure and then fuel injected to the cylinder where the fuel is self-ignited due to high temperature by compression. The process is thus called as compression ignition. In this cycle, the heat is transferred to the fluid at constant pressure.

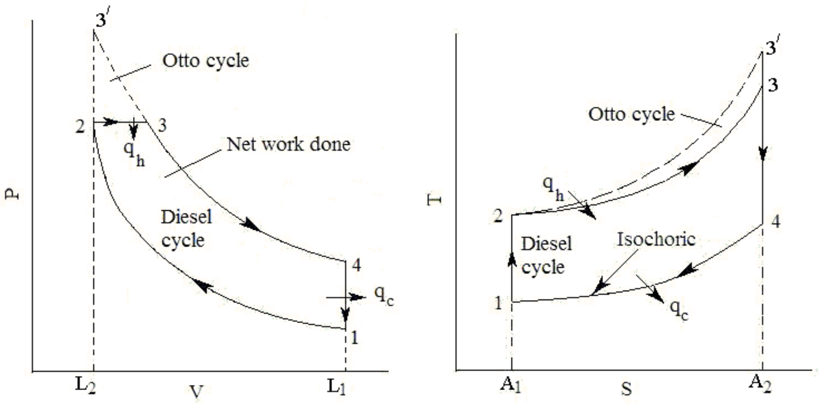


Fig. 52. Diesel cycle on P-V and T-S diagram.

In Diesel cycle, air is taken into the cylinder and is undergone reversible and adiabatic reversible, i.e. isentropic compression from state-1 to state-2. It is shown in the P-V and T-S diagrams. Then oil is sprayed into the cylinder and it ignites. In the process from state-2 to state-3, it receives the heat q_h at constant pressure. Then the combustion gases undergo the isentropic expansion from state-3 to state-4 with the increase in volume. In the next stroke, the constant volume cooling is performed from 4 to 1 by removing heat (q_c). Next the cycle is continued.

In Diesel engine, the amount of work required will be less by the area 23’3 in the P-V diagram. So this engine is economic.

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