

### Unit III

## **ENERGY SOURCES AND BATTERY TECHNOLOGY**

### **FUELS – Introduction**

#### **Definition**

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

**Eg:** Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas, etc., are some of the fuels.

During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to “rearrangement of valency electrons” in these atoms, resulting in the formation of new compounds like  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. These new compounds have less energy in them and therefore, the energy (or heat) released during the combustion process is the difference in the energy of the reactants and that of the products formed.



The primary or main source of fuels is coals and petroleum oils, the amounts of which are diminishing day-by-day. These are stored fuels available in earth's crust and are generally called “fossil fuels”.

### **Classification of Fuels**

Fuels are broadly classified according to their-

- Occurrence
- State of aggregation

According to the first classification, we have:

**1. Natural or primary fuels** - which are found in nature as such.

Eg: Wood, peat, coal, petroleum, natural gas, etc.

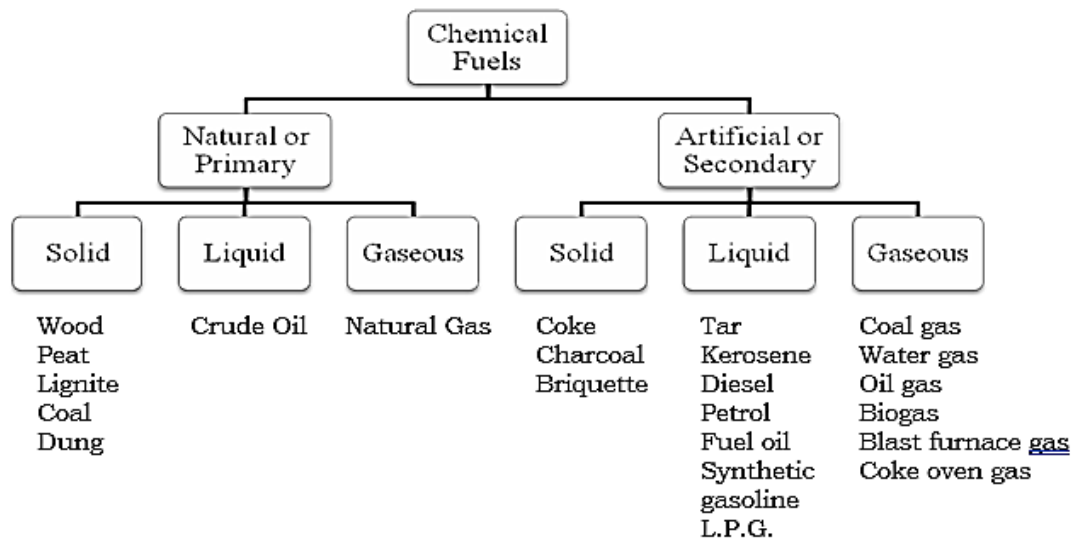
**2. Artificial or secondary fuels** - which are prepared from the primary fuels.

Eg: Charcoal, coke, kerosene oil, diesel oil, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.

According to the second classification, we have –

- 1. Solid,**
- 2. Liquid and**
- 3. Gaseous fuels**

The Classification of fuels is summarized as follows:



## **Calorific Value**

Calorific value of a fuel is “the total quantity of heat liberated, when a unit mass of the fuel is burnt completely”.

### **Units of heat**

- Calorie (cal)
- Kilocalorie (kcal)
- British thermal unit (B.Th.U.)
- Centigrade Heat Unit (C.H.U.)

## **Characteristics of a Good Fuel**

- 1. High Calorific value:** A fuel should possess high calorific value. Since the amount of heat liberated and temperature attained thereby depends upon the calorific value of fuel.
- 2. Moderate ignition temperature:** Ignition temperature is the lowest temperature to which the fuel must be pre-heated so that it starts burning smoothly. Low ignition temperature is dangerous for storage and transport as it can catch fire. On the other hand, high ignition temperature causes difficulty in igniting the fuel, but the fuel can be safely stored, handled, and transported. Hence, an ideal fuel should have moderate ignition temperature.
- 3. Low moisture content:** The moisture content of the fuel reduces the heating value and possess low calorific value which involves loss of money. Hence, fuel should have low moisture content.
- 4. Low non-combustible matter content:** After combustion, the non-combustible matter remains generally in the form of ash or clinker. The non-combustible matter also reduces the calorific value of a fuel and the disposal of waste product produced is another problem. Thus, a good fuel should have low content of non-combustible matter.

- 5. Moderate velocity of combustion:** The rate of combustion of a fuel should be moderate and uniform. If the rate is low, a part of the heat liberated may get radiated before raising the temperature.
- 6. Products of combustion should not be harmful:** Fuel on burning should not give out toxic or poisonous gases like,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , etc. which will pollute the atmosphere.
- 7. Low costs:** A good fuel should be readily available in bulk at low cost.
- 8. Easy to transport:** Handling and transport of a fuel should be easy. Thus, solid, and liquid fuels are better than gaseous fuels which can cause fire hazards.
- 9.** The combustion of the fuel should be easily controllable, i.e., it should be easy to start or stop when required.
- 10.** It should not ignite spontaneously which can cause fire accidents.
- 11.** It should burn in air with efficiency without liberating much smoke.
- 12.** The combustion should be regular and uniform. Thus, in case of solid fuel the size should be uniform.

## Coal

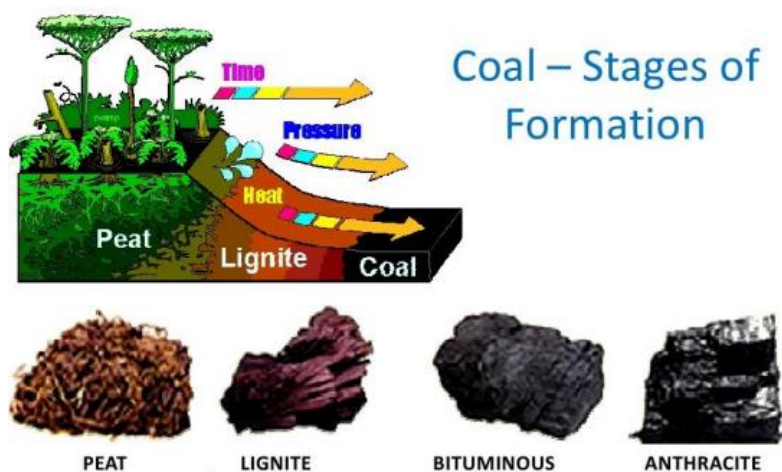
Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions like temperature, pressure, and bacterial action over a period of thousands of years. It is chiefly composed of C, H, N and O besides non-combustible inorganic matter.

The process of conversion of wood into coal is called coalification. Depending upon the percentage of carbon, hydrogen, moisture, and calorific value, four different types of coal exist. It is called the ranking of coal.

The successive stages in the transformation of vegetable matter into coal are – wood, peat, lignite, bituminous coal, and anthracite.

The progressive transformation of wood to anthracite results in increase in carbon content, hardness and calorific value and decrease in volatile matter, moisture, and H, O, N, and S contents.

Anthracite is probably the purest form of coal and contains 95 % carbon.



## Analysis of Coal

The quality of coal can be measured by the following two types of analysis:

**Proximate Analysis:** It involves in the following determinations:

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

$$\% \text{ of moisture} = \frac{\text{Loss in weight}}{(\text{wt. of coal taken})} * 100$$

**Importance:** Moisture in coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel. Moisture up to 10% produces a more uniform fuel bed and less of “fly-ash”.

- 2. Volatile matter:** The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in a muffle furnace, maintaining at 925°±20°C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage basis.

$$\% \text{ of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{(\text{wt. of coal sample taken})} * 100$$

**Importance:** A high volatile matter content means that a high proportion of fuel will distill over as gas or vapour, a large proportion of which escapes unburnt. So, higher volatile content in coal is undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of coal.

- 3. Ash:** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at 700°±50°C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccator and weighed. Heating, cooling, and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage basis.

$$\% \text{ of ash} = \frac{\text{Wt. of ash left}}{(\text{wt. of coal taken})} * 100$$

**Importance:** Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. It blocks the passages. The presence of ash increases transporting, handling, storage, and disposal costs.

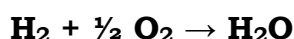
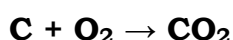
#### 4. Fixed carbon:

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

**Importance:** Higher the percentage of fixed carbon, greater is its calorific value and better the quality of coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. The percentage of fixed carbon helps in designing the furnace and the shape of the firebox, because it is the fixed carbon that burns in the solid state.

**Ultimate analysis:** It involves in the following determinations:

- 1. Carbon and Hydrogen:** About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively.



The gaseous products of combustion are absorbed respectively in KOH and  $\text{CaCl}_2$  tubes of known weights. The increase in weights of these are then determined.

$$\% \text{ of carbon} = \frac{\text{Increase in wt. of KOH tube} * 12 * 100}{(\text{wt. of coal sample taken} * 44)}$$

Where, 12 represent the atomic weight of C and 44 represents the molecular weight of  $\text{CO}_2$ .

$$\% \text{ of hydrogen} = \frac{\text{Increase in wt. of CaCl}_2 \text{ tube} * 2 * 100}{(\text{wt. of coal sample taken} * 18)}$$

Where, 2 is the molecular weight of  $\text{H}_2$  and 18 is the molecular weight of  $\text{H}_2\text{O}$ .

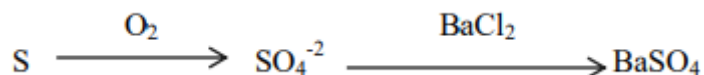
**Importance:** Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter. So, lesser the percentage of hydrogen better is the quality of coal. The percentage of carbon forms the basis of classification of coal. Higher the percentage of carbon, higher the calorific value of coal.

- 2. Nitrogen:** About 1 g of accurately weighed powdered coal is heated with concentrated  $\text{H}_2\text{SO}_4$  along with  $\text{K}_2\text{SO}_4$  catalyst in a Kjeldahl's flask. After solution becomes clear, it is treated with excess of KOH and the liberated ammonia is allowed to absorb in a known volume of standard acid solution. The unused acid is titrated against standard alkali. From this we can calculate the volume of acid reacted with ammonia.

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} * \text{normality} * 1.4}{(\text{wt. of coal taken})}$$

**Importance:** Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little nitrogen content.

**3. Sulphur:** It is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution when barium sulphate is precipitated. This precipitate is filtered, washed, and heated to constant weight.



$$\% \text{ of sulphur} = \frac{\text{Wt. of BaSO}_4 \text{ obtained} * 32 * 100}{(\text{wt. of coal sample taken in bomb} * 233)}$$

Where, 32 is the atomic weight of sulphur and 233 is the molecular weight of BaSO<sub>4</sub>.

**Importance:** Sulphur although contributes to the heating value of coal, yet on combustion produces acids and oxides of sulphur which pollutes the atmosphere and leads to corrosion. Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel.

**4. Ash:** Ash determination is carried out as in proximate analysis.

**5. Oxygen:**

$$\% \text{ of oxygen} = 100 - \% \text{ of (C + H + S + N + ash)}$$

**Importance:** Oxygen content decreases the calorific value of coal. High oxygen content coals are characterized by high inherent moisture, low calorific value, and low coking power. Oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

### Crude Oil or Petroleum

Petroleum or crude oil is the main source of liquid fuels. 60% of the world reserves of petroleum are in the Middle East while 15% are in the Western hemisphere.

The word petroleum is derived from the two Latin words, *Petra* (=rock) and *Oleum* (=oil). So, it is also known as crude oil or rock oil or mineral oil. It is a dark coloured viscous liquid found deep in the earth's crust. It is a complex mixture of hydrocarbons (e.g., paraffinic, olefinic and aromatic) with small quantity of optically active organic compounds containing O, N and S and traces of metallic constituents.

## **Mining of petroleum**

In order to bring the crude oil to the surface, pipes are sent through the drilled holes into the oil wells or pumped out with the help of air –lift pumps.

## **Refining of Petroleum/Processing of petroleum**

Crude oil coming out from the well generally consists of a frothing mixture of solid, liquid, and gaseous hydrocarbons containing sand and water in suspension.

The crude oil is separated into various useful fractions by fractional distillation. These fractions are finally converted into desired specific products by removing objectionable impurities. The process is called ‘refining of crude oil’ and the plants set up for the purpose, are called oil refineries.

The process of refining involves the following steps:

- Removal of solid impurities
- Separation of water (Cottrell’s process)
- Removal of harmful sulphur compounds
- Fractional distillation

### **Step-1: Removal of solid impurities**

Crude oil is a mixture of solid, liquid, and gaseous substances. This is allowed to stand undisturbed for some time when heavy solid particles settle down and gases evaporate. The supernatant liquid is then centrifuged wherein the solids get removed.

### **Step-2: Separation of water (Cottrell’s process)**

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

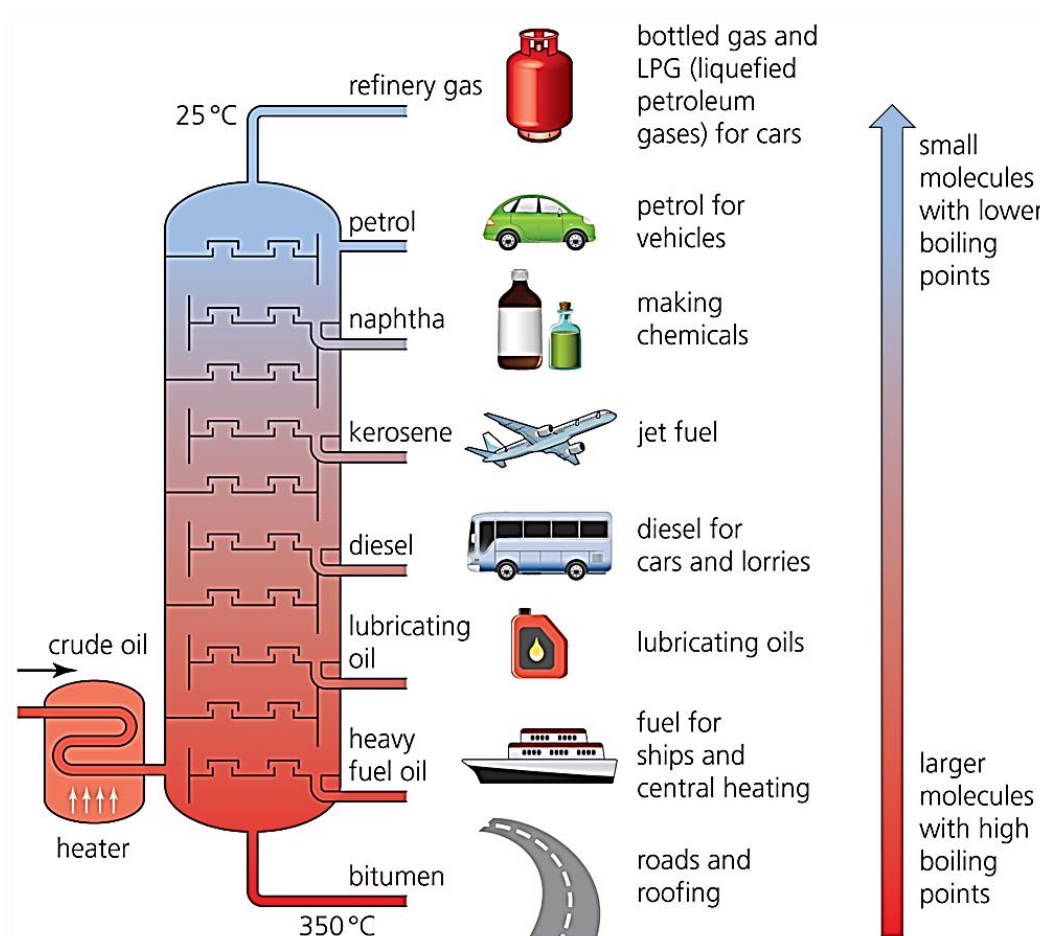
### **Step-3: Removal of harmful sulphur compounds**

This involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide (a solid), which is then removed by filtration.

### **Step-4: Fractional distillation**

The crude oil is heated to about 400°C in a pipe still whereby all volatile constituents are evaporated. The hot vapours are then passed through a tall cylindrical tower called fractionating column, containing a number of horizontal stainless-steel trays at short distances. Each tray is provided with small chimney, covered with a loose cap. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column.

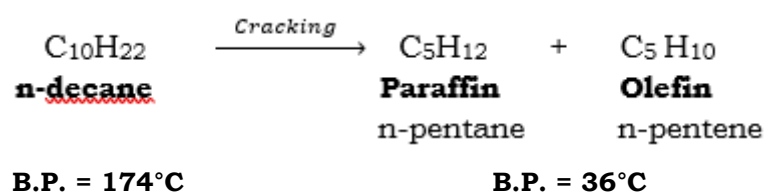
Higher boiling fraction condenses first, while the lower boiling fractions condense later as shown in the figure.



## Cracking

The mixture of light hydrocarbons which is obtained by distillation is called “straight run gasoline” and consists mainly of straight chain molecules. However, the gasoline obtained by fractional distillation is not of very good quality. So to get improved gasoline a process of thermal decomposition known as cracking is used.

**Definition:** Cracking is defined the decomposition of higher molecular weight hydrocarbons if high boiling points into simpler, lower molecular weight hydrocarbons of low boiling points.



There are two methods of cracking in use:

1. Thermal cracking
2. Catalytic cracking



## Thermal cracking

The heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins plus some hydrogen. This process may be carried out either in liquid-phase or vapour-phase.

**Liquid phase thermal cracking:** The heavy oil or the gas oil stock is cracked at  $475-530^{\circ}\text{C}$  and under high pressure of  $100\text{ Kg/cm}^2$ . The cracked products are separated in a fractionating column. The octane rating of the petrol produced is about 65-70.

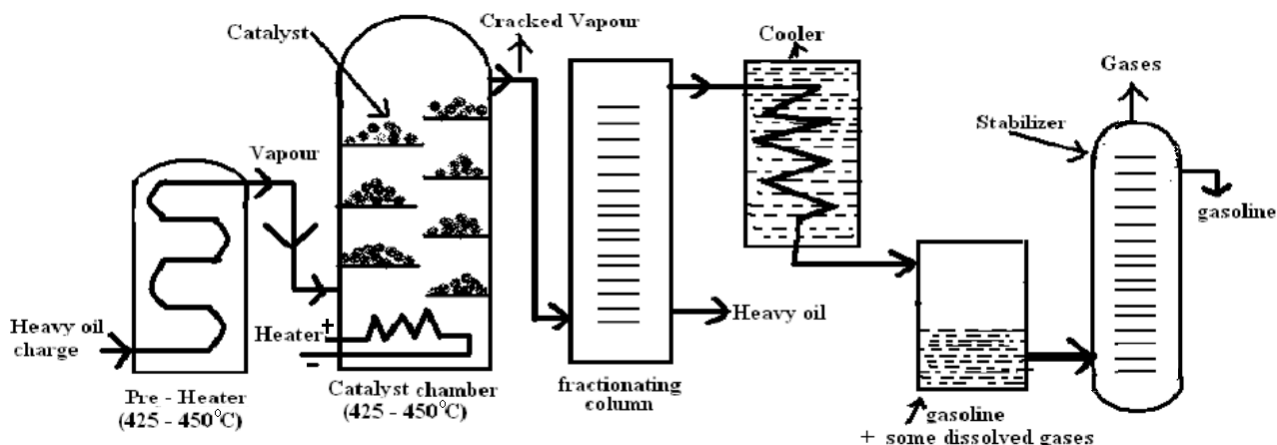
**Vapour phase thermal cracking:** The cracking oil is first vapourised and then cracked at about  $600-650^{\circ}\text{C}$  and under a low pressure of  $10-20\text{ kg/cm}^2$ . This process is suitable only for those oils, which may be readily vaporized. It requires less time than the liquid-phase method. Petrol obtained from vapour-phase cracking has better anti-knock properties, but poorer stability than petrol from liquid-phase cracking.

## Catalytic cracking

A better quality and yield are obtained by this process compared to thermal cracking. The cracking is carried out in the presence of a catalyst - Aluminium silicate,  $\text{Al}_2(\text{SiO}_3)_3$  or alumina  $\text{Al}_2\text{O}_3$ .

There are two methods of catalytic cracking in use:

**Fixed bed catalytic cracking:** The heavy oil charge is passed through a pre-heater where it is heated up to  $420-450^{\circ}\text{C}$ . The hot vapours are then passed over a fixed bed of catalytic chamber maintained at  $425-450^{\circ}\text{C}$  and  $1.5\text{ kg/cm}^2$  pressure.



During this passage through the tower, about 40 % of the charge is converted into gasoline and about 2-4 % carbon is formed. The latter gets adsorbed on the catalyst bed. The vapours produced are then passed through a fractionating column, where heavy oil fractions condense. The vapours are then led through a cooler, where some of the gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is

The catalyst after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activation interval, the vapours are diverted through another catalyst chamber.

10

The catalyst powder gradually becomes heavier due to the deposition of carbon and settles at bottom. This is forced into the regenerator. In this regenerator carbon is burnt off and catalyst is regenerated or reactivated and again sent into reacting tower through hopper.

The gases from the fractionating towers are sent into condenser and then to stabilizer to recover gasoline.

## **Knocking**

In an internal combustion engine, a mixture of gasoline vapour and air in a fixed ratio (1:17) is used as a fuel. This mixture is compressed and ignited by an electric spark. After initiation of the combustion reaction by spark in the cylinder the flame should spread rapidly and smoothly through the gasoline mixture, thereby the expanding gas drives the piston down the cylinder. The fuel-air mixture is compressed. The efficiency of an internal combustion engine increases with the compression ratio [ratio of gasoline volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke of the piston].

But in certain circumstances the rate of oxidation of hydrocarbons is so great that the last portion of the oil and air mixture is ignited instantaneously which is called pre-ignition producing an explosive sound called knocking or Engine knock. The knocking results in loss of efficiency. So, knocking results in decreased power output but can also cause mechanical damage by overheating of the cylinder parts.

The chemical structure of the petrol is responsible for knocking. The tendency of fuel constituents to knock is in the following order:

**Straight chain paraffins (n-paraffins) > branched chain paraffins (iso paraffins) > olefins > cycloparaffins (naphthalenes) > aromatics.**

Thus, olefins of the same carbon chain length possess better antiknock properties than the corresponding paraffins and so on.

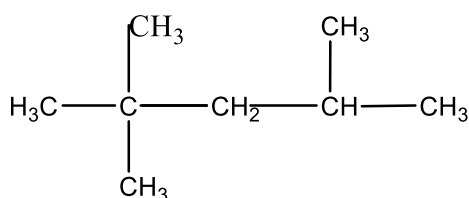
The extent of knocking of petrol is measured by a test called octane rating or octane number.

## **Octane Number**

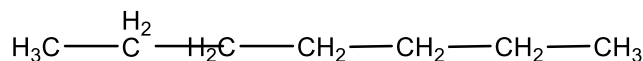
Edger introduced the term Octane Number to explain the knocking characteristics of combustion engine fuel. The Octane Number of a fuel is a measure of its ability to resist knocking. A fuel with high octane number has the greatest resistance to spontaneous combustion/ignition.

The octane number of gasoline is defined as the percentage of iso-octane present in a mix of iso-octane and n-heptane. n-Heptane knocks very badly and hence its anti-knocking value is arbitrarily given as zero. Whereas iso-octane gives very little knocking and so its anti-knocking value is taken as 100. Greater the octane number greater is the resistance to knocking.

The octane number of gasoline is numerically taken as the % by volume of iso-octane in a mix of iso-octane and n-heptane, which just matches with the knocking characteristics of the fuel under testing.



2,2,4-trimethyl pentane (iso-octane)



n-heptane

Thus, if a sample of petrol gives as much of knocking as a mix of 75 parts of iso-octane and 25 parts of n-heptane, then its octane number is 75. Olefins have higher antiknock property than the corresponding paraffins. Aromatic hydrocarbons such as benzene and toluene have high octane numbers.

The octane number of fuels can be raised by the addition of certain compounds like tetra ethyl lead  $[(\text{C}_2\text{H}_5)_4\text{Pb}]$  or TEL, diethyl telluride  $[(\text{C}_2\text{H}_5)_2\text{Te}]$ .

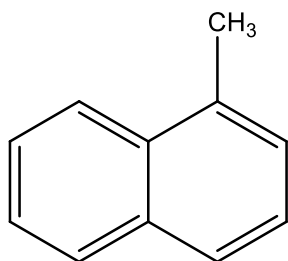
Such compounds are called anti-knock compounds and the process is called doping.

TEL gives rise to Pb and PbO during combustion. These particles act as free-radical chain inhibitors as they arrest the propagation of the explosive chain reactions possible for knocking.

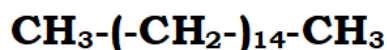
Methyl tertiary butyl ether (MTBE) can also be added to improve the octane rating of the fuel. MTBE has oxygen in the form of ether group and supplies oxygen for the combustion of the petrol in IC engine thus reducing the formation of peroxy compounds.

## Cetane Number

In diesel engines the fuel is exploded by the application of heat and pressure and not a spark. The interval between the start of fuel injection and the ignition is called ignition delay and is an important quality of diesel fuel. If the ignition delay is long, it is responsible for diesel knocking. In order to avoid diesel knock, the ignition delay period should be as short as possible, and these diesel fuels are graded by means of cetane ratings. So, the knocking characteristics are referred as cetane number. Cetane number of diesel oil is defined as the percent by volume of cetane in a mix of cetane and  $\alpha$  - methyl naphthalene. Cetane (n-hexadecane) having a very short ignition delay is given the value of 100 in the rating scale.  $\alpha$  - methyl naphthalene having a longer ignition delay represents zero of the scale.



**2-methyl naphthalene**  
**Cetane number = 0**



**n-hexadecane**  
**Cetane number = 100**

High cetane number fuels eliminate diesel knock and can be increased by adding certain organic additives such as ethyl nitrite, isoamyl nitrite and acetone peroxide. So, diesel knocking may be minimized.

## Gaseous fuels

### Types of Hydrogen fuel

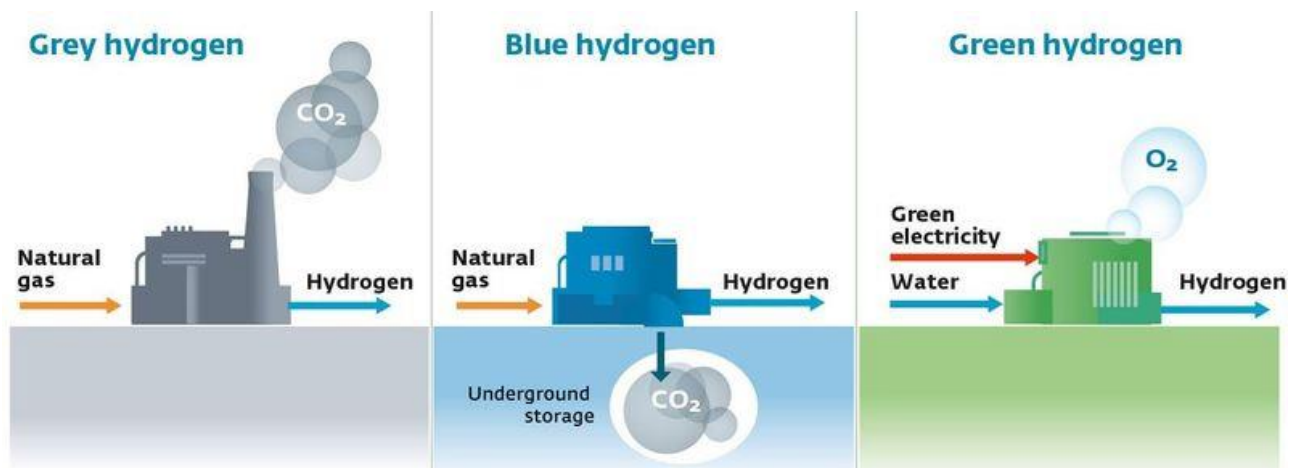
Hydrogen is an abundant element that is currently produced in molecular form for a wide range of industrial uses. In recent years, it is also starting to be used for stationary power production in fuel cell systems and to power fuel cell electric vehicles including buses, forklifts, and passenger cars. One highly compelling attribute of hydrogen is that it can be produced in many different ways and using a variety of feedstocks.

A range of potential hydrogen production methods and pathways are available. These include reformation, gasification, electrolysis, and other advanced processes. Depending on the production pathway hydrogen fuel can be classified into various types.

**Green hydrogen:** It is produced through water electrolysis process by employing renewable electricity. The reason it is called green is that there is no CO<sub>2</sub> emission during the production process. Water electrolysis is a process that uses electricity to decompose water into hydrogen gas and oxygen.

**Blue hydrogen:** It is sourced from fossil fuel (natural gas), the CO<sub>2</sub> is captured and stored underground (carbon sequestration). Companies are also trying to utilize the captured carbon called carbon capture, storage and utilization (CCSU). As no CO<sub>2</sub> is emitted, so the blue hydrogen production process is categorized as carbon neutral.

**Grey hydrogen:** It is produced from fossil fuel (natural gas) and commonly uses steam methane reforming (SMR) method. During this process, CO<sub>2</sub> is produced and eventually released to the atmosphere.



**Black/Brown hydrogen:** They are produced from coal. The black and brown colours refer to the type bituminous (black) and lignite (brown) coal. The gasification of coal is a method used to produce hydrogen. CO and CO<sub>2</sub> are byproducts released into atmosphere.

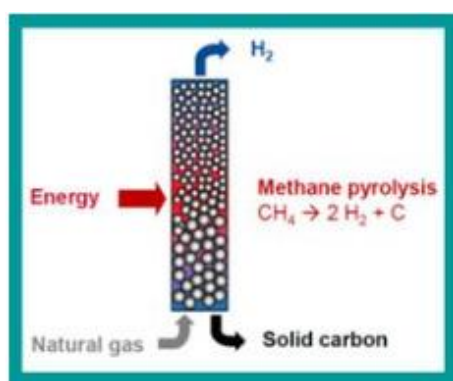


Bituminous coal is used to  
make black hydrogen



Brown coal (lignite) is used to  
make brown hydrogen.

**Turquoise hydrogen:** It can be extracted by using the thermal splitting of methane via methane pyrolysis. The process though at the experimental stage, remove the carbon in a solid form instead of CO<sub>2</sub> gas.



Methane pyrolysis is used to  
make turquoise hydrogen.

**Purple hydrogen:** It is made using nuclear power and heat through combined thermochemical water splitting (high temperature electrolysis).

**Pink hydrogen:** It is generated through electrolysis of water by using electricity from a nuclear power plant.

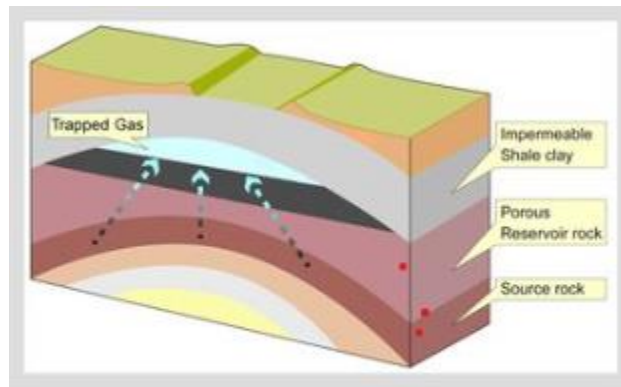


Nuclear power is used to  
make pink hydrogen.

**Red hydrogen:** It is produced through the high temperature catalytic splitting of water using nuclear thermal power as an energy source.

**White hydrogen:** It refers to naturally occurring geological hydrogen that might be (rarely) found in underground deposits.





Naturally occurring geological hydrogen is called white hydrogen.

**Yellow hydrogen:** It indicates hydrogen produced via electrolysis through solar energy. However, it is also used to indicate that the electricity used for the electrolysis comes from mixed sources. This mix of sources comes from the electrical grid and is based on availability and can range from renewables to fossil fuels.



Solar power or a mix of energy sources from the electrical grid are used to make yellow hydrogen.

## **Methods of hydrogen production**

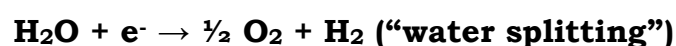
Methods of Hydrogen production involves:

- Steam methane process
- Gasification process
- Hydrocarbon Pyrolysis
- **Electrolysis of water**

## **Electrolysis of water**

Electrolysis is the process through which water molecules are split into hydrogen and oxygen molecules using electricity and an electrolyzer device. Electrolyzers are effectively fuel cell devices that operate in reverse.

The overall electrolysis reaction is:



Hydrogen can be produced via electrolysis of water from any electrical source, including utility grid power, solar photovoltaic (PV), wind power, hydropower, or nuclear power.

## Mechanism of water electrolysis

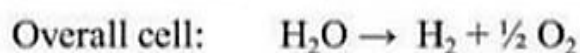
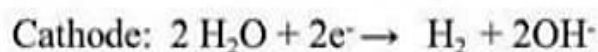
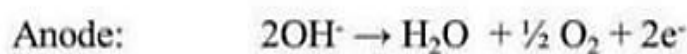
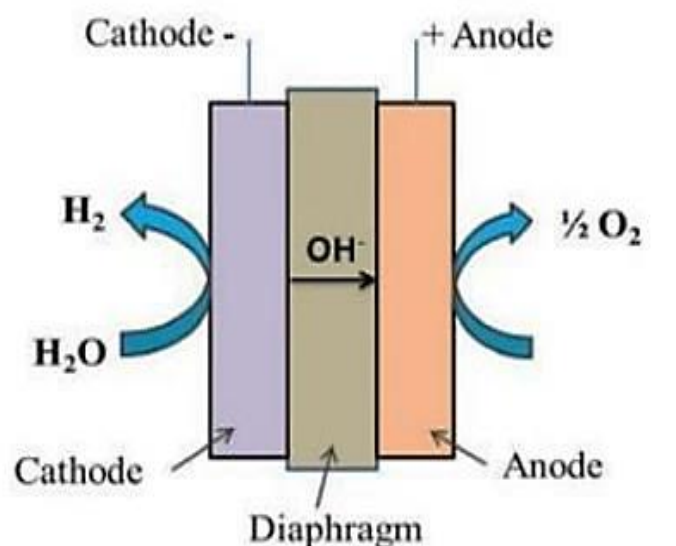
In water electrolysis process, electrolyser is a system that uses electricity to break water into hydrogen and oxygen. Through electrolysis, the electrolyzer system creates hydrogen gas. The oxygen that's left over is released into the atmosphere or can be captured or stored to supply other industrial processes or even medical gases in some cases.

An electrolyser contains a cathode (negative charge), an anode (positive charge) and a membrane. The entire system also contains pumps, vents, storage tanks, a power supply, separator, and other components. Water electrolysis is an electrochemical reaction which takes place within the cell stacks. Electricity is applied to the anode and cathode across the proton exchange membrane (PEM) and causes the water ( $\text{H}_2\text{O}$ ) to split into its component molecules, hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ).

## Types of Electrolysers

### Alkaline electrolyser

They use a liquid electrolyte solution, such as potassium hydroxide or sodium hydroxide, and water. Hydrogen is produced in a cell consisting of an anode, a cathode and a membrane. The cells are usually assembled in series to produce more hydrogen and oxygen at the same time. When current is applied to the electrolysis cell stack, hydroxide ions move through the electrolyte from the cathode to the anode of each cell, generating bubbles of hydrogen gas on the cathode side of the electrolyser and oxygen gas at the anode.

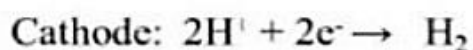
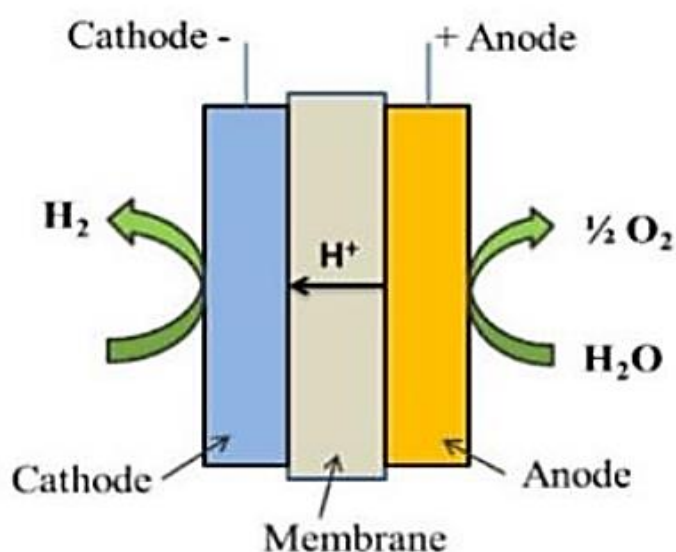




They have been in use for more than 100 years and do not require noble metals as a catalyst; however, they are bulky equipment that obtains medium purity hydrogen and are not very flexible in operation.

### **Proton exchange membrane (PEM) electrolyser**

PEM electrolyzers use a proton exchange membrane and a solid polymer electrolyte. When current is applied to the battery, water splits into hydrogen and oxygen and the hydrogen protons pass through the membrane to form hydrogen gas on the cathode side. They are the most popular because they produce high-purity hydrogen and are easy to cool. But, they are somewhat more expensive because they use precious metals as catalysts.

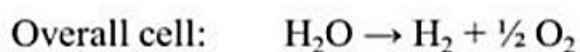
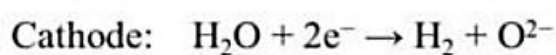
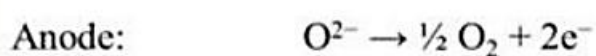
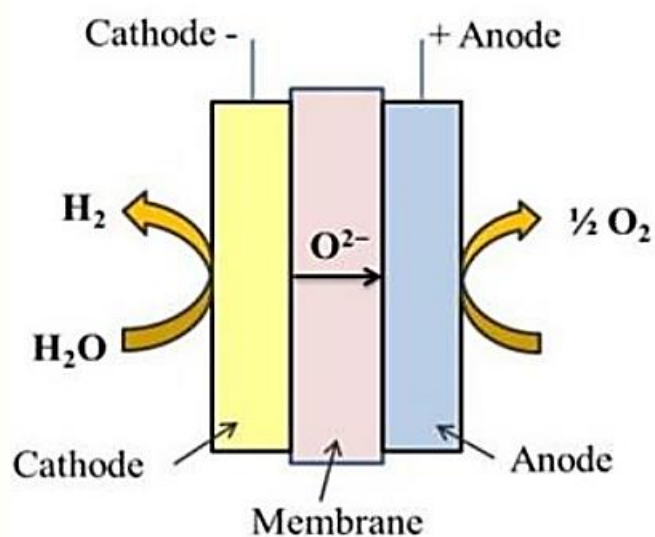


### **Solid oxide electrolysis cell (SOEC)**

SOECs operate at a higher temperature (between 500 and 850°C) and have the potential to be much more efficient than PEMs and alkaline electrolyzers. The process is called high-temperature electrolysis (HTE) or steam electrolysis and uses a solid ceramic material as the electrolyte. Electrons from the external circuit combine with water at the cathode to form hydrogen gas and negatively charged ions. Oxygen then passes through the sliding ceramic membrane and reacts at the anode to form oxygen gas and generate electrons for the external circuit. Technologically they are less developed than the above.

There are other types of electrolyzers that are not yet as efficient or cost-effective as the above but have a lot of potential for development.

One example is photo electrolysis, which uses only sunlight to separate water molecules without the need for electricity. However, this device requires semiconductors that have not yet been sufficiently developed.



### Basic chemical reactions and operating temperature range for different types of water electrolysis techniques

Electrolysis technology	Alkaline Electrolysis	Membrane Electrolysis	High Temperature Electrolysis
Anode Reaction Oxygen Evolution Reaction (OER)	$2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^-$	$H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$	$O^{2-} \rightarrow \frac{1}{2} O_2 + 2e^-$
Cathode Reaction Hydrogen Evolution Reaction (HER)	$H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Charge carrier	$OH^-$	$H^+$	$O^{2-}$
Operating Temperature Range	40 – 90 °C	20 – 100 °C	700 – 1000 °C

## **BATTERY TECHNOLOGY**

### **Batteries**

**Definition:** A device that stores chemical energy that later release energy as electricity is called a battery.

It may be alternatively defined as an electrochemical cell or often, several electrochemical cells connected in a series that can be used as a source of direct electric current at a constant voltage.

### **Characteristics of a good battery**

A single battery may not exhibit all good characteristics, but a battery can be designed and constructed with specific characteristics for a particular application. Some of the important characteristics of a battery are:

**1. High capacity**, which is very small variation of voltage during discharge.

**2. High energy efficiency**, which is calculated as

$$\% \text{ of efficiency} = \frac{\text{energy released on discharge}}{\text{energy required for charge}} \times 100$$

**3. High cycle life**, which is the number of charging and discharging cycles before failure.

**4. Long shelf life.**

**5. Tolerance to different service conditions** such as variation in temperature, vibration shock, etc.

**6. Reliability.**

**7. Affordable price.**

**8. Fast charging.**

**9. Compact and light weight.**

**10. Portable.**

### **Classification of batteries**

Batteries can be classified into four types:

**1. Primary battery or primary cells:** These are not rechargeable batteries, because the cell reactions are irreversible. When most of the reactant parts have been converted to products, no more electricity is produced, and the battery becomes dead. They have to be discarded after the use. Such batteries are called primary batteries.

**E.g.:** Zn-MnO<sub>2</sub> battery, Dry cell, Mercury battery, Zn-Air battery, etc.

**2. Secondary Battery or secondary cells:** These are rechargeable batteries, because the cell reactions are reversible. They are also called storage batteries, as they are the storage devices for electrical energy. The discharged cell can be recharged by passing current through it in the direction opposite to that of

discharge current. Thus, a secondary battery may be used through a large number of cycles of discharging and charging.

**E.g.:** Lead – Acid Battery, Ni-Cd battery, NiMH battery, Li ion battery, etc.

**3. Reserve Batteries:** Reserve batteries have long shelf life and extreme storage. In this type of battery, one of the components is stored separately and is incorporated into the battery when required; usually the electrolyte is the component that is isolated. This battery structure is commonly observed in thermal batteries, whereby the electrolyte remains inactive in a solid state until the melting point of the electrolyte is reached, allowing for ionic conduction, thus activating the battery. Reserve batteries effectively eliminate the possibility of self-discharge and minimize chemical deterioration. Most reserve batteries are used only once and then discarded.

Reserve cells are typically classified into the following 4 categories.

- Water activated batteries.
- Electrolyte activated batteries.
- Gas activated batteries.
- Heat activated batteries.

**E.g.:** Magnesium batteries activated by water (Mg–AgCl and Mg–CuCl)

It is used to deliver high power for relatively short periods of time in applications such as missiles, torpedoes, and other weapon systems.

**4. Flow battery or fuel cells:** In fuel cells, materials (reactants, products, and electrolytes) pass through the battery. It is simply an electrochemical cell that converts chemical to electrical energy. They do not store energy. But energy can be withdrawn indefinitely as long as outside supply of fuel is maintained.

**E.g.:** Hydrogen-oxygen fuel cell, Methanol-oxygen fuel cell.

## **Primary batteries**

### **Zn-Air battery**

Zinc-air battery is a primary battery. It is a non-rechargeable battery. Cell reactions are irreversible.

#### **Construction:**

Anode: Granulated zinc

Cathode: Porous carbon plate

Electrolyte: KOH

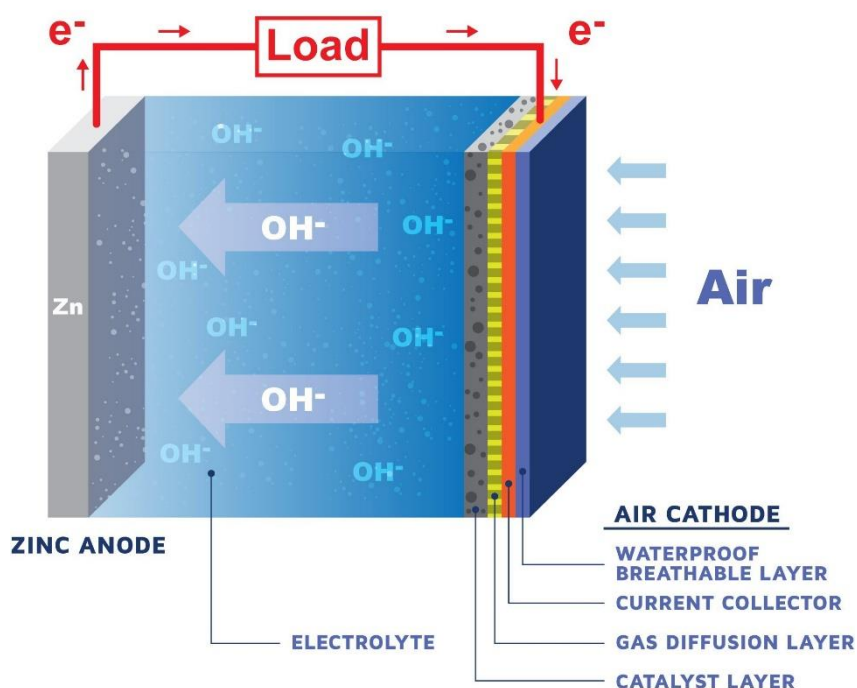
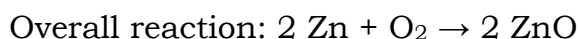
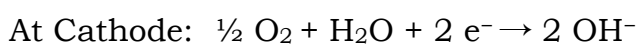
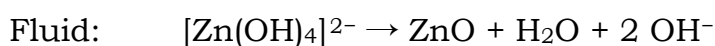
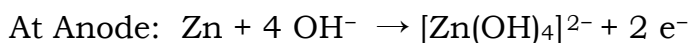
Zinc-air battery is represented as  $\text{Zn} \mid \text{KOH} \parallel \text{Air, C}$

- Cathode is made up of porous plate of carbon which is activated by MnO.

- Anode is made up of rectangular pellets of zinc and is enclosed between two carbon plates. Electrolyte is aqueous KOH. Hence it is also called as alkaline battery.
- Electrodes are separated by a separator and the whole assembly is enclosed in a glass container or ebonite container coated with gas permeable Teflon coating which is hydrophobic so that it allows only oxygen in the air to pass through and repels back water, i.e., moisture.

### Working:

Zn-air batteries generate electricity through the electrochemical reaction of Zn and oxygen. During discharge of the battery, Zn anode is oxidized and produces zincate and the latter changes to zinc oxide. At the cathode, oxygen from the atmosphere undergoes reduction. The cell voltage for the chemistry is theoretically capable of 1.65 Volts however almost all designs are optimised for less than 1.4 or 1.3 Volts in order to achieve longer lifetimes.



### Advantages:

- High energy density but low power.
- Inexpensive materials.
- The zinc-air system, when sealed, has excellent shelf life, with a self-discharge rate of only 2 percent per year.
- Primary cells available in a range of button and coin cell sizes.
- Rechargeable high-power cells available for traction applications.

**Disadvantages:**

- Sensitive to extreme temperature and humid conditions.
- Carbon dioxide from the air forms carbonate which reduces conductivity.
- High self-discharge.
- After activation, chemicals tend to dry out and the batteries have to be used quickly.
- Although recharging is possible it is also inconvenient and is only suitable for high power types.

**Applications:**

- Used in power source in hearing aid.
- Used in electronic pagers.
- Used in military radio services.
- Used in voice transmitters.
- Used in remote communications.
- Used in railroad signalling.

**Rechargeable batteries****Lithium-ion battery**

Lithium-ion batteries are secondary batteries. They are rechargeable. They are common in home electronics. They are growing in popularity due to its light weight, high energy density, ability to recharge and low self-discharge.

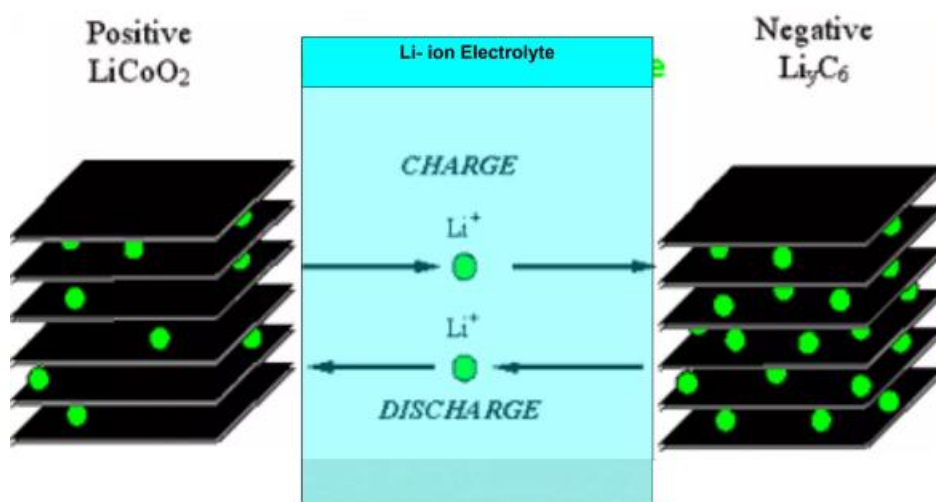
**Construction:**

Anode: Graphite intercalated with Lithium ions ( $\text{Li}_x\text{C}_6$ ) (with thin Cu foil as current collector).

Cathode: Lithium cobalt oxide ( $\text{LiCoO}_2$ ) (with thin Al foil as current collector).

Electrolyte: A lithium salt such as  $\text{LiPF}_6$  dissolved in binary organic solvent mixture (such as ethylene carbonate – dimethyl carbonate).

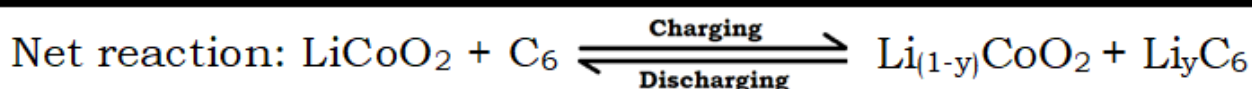
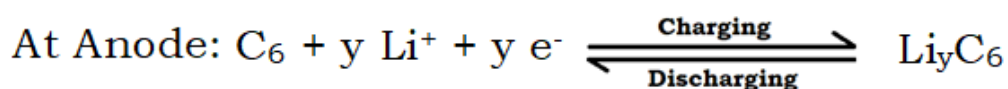
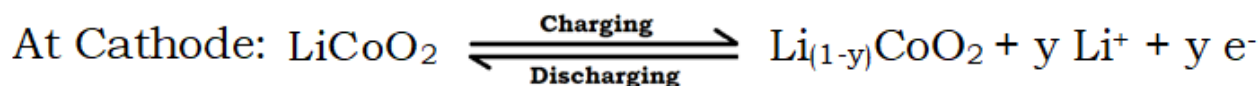
Separator: Fine porous polymer film.

**Principle:**

During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers of the electrodes through lithium electrolyte.

### Working:

- Lithium ion battery depends on an “intercalation” mechanism. This involves the insertion of lithium ions into the crystalline lattice of the host electrode without changing its crystal structure.
- These electrodes have two key properties. One is the open crystal structure, which allow the insertion or extraction of lithium ions and the second is the ability to accept compensating electrons at the same time. Such electrodes are called intercalation hosts.
- During charging, lithium in positive electrode material is ionized and moves from layer to layer and inserted into the negative electrode.
- During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode.
- At the same time, the compensating electrons travel in the external circuit and are accepted by the host to balance the reaction.
- The process is completely reversible. Thus, the lithium ions pass back and forth between the electrodes during charging and discharging.
- Because of this reason, the lithium ion batteries are called ‘Rocking chair’ or ‘Swing’ cells.



### Advantages:

- They have high energy density than other rechargeable batteries.
- They are less in weight.
- They produce high voltage out about 3.6 V as compared with other batteries.
- They have improved safety, i.e., more resistance to overcharge.
- No liquid electrolyte means they are immune from leaking.
- Fast charge and discharge rate.
- Low self-discharge.

### Disadvantages:

- They are expensive.
- They are not available in standard cell types.
- Electrolyte breakdown into flammable gases by overheating.

### **Applications:**

- The Li-ion batteries are used in cameras, calculators, smart phones, and most of the consumer electronics device.
- They are used in cardiac pacemakers and other implantable device.
- **Electric vehicles:** Because of their light-weight Li-ion batteries are used for propelling a wide range of electric vehicles such as aircraft, electric cars, hybrid vehicles, advanced electric wheelchairs, radio-controlled models, model aircraft and the Mars Curiosity rover.
- **Power tools:** Li-ion batteries are used in tools such as cordless drills, sanders, saws, and a variety of garden equipment including whipper-snippers and hedge trimmers.

### **Fuel Cell**

#### **Definition**

A fuel cell is an electrochemical cell which converts chemical energy contained in an easily available fuel-oxidation system into electrical energy.

E.g.: H<sub>2</sub>-O<sub>2</sub> Fuel cell, Methanol-O<sub>2</sub> fuel cell, etc.

The basic principle of fuel cells is identical to those of the well-known electrochemical cells, the only difference is that in fuel cell the chemical energy is provided by a fuel and an oxidant stored outside the cell.

The fuel and the oxidizing agents are continuously and separately supplied to the electrodes of the cell, at which they undergo reactions.



Fuel cells are capable of supplying current as long as the outside supply of fuel is maintained.

#### **Characteristics**

- They have high efficiency.
- Their noise levels are low.
- They are free from vibration, heat transfer and thermal pollution.
- They are modular and hence can be built-in a wide range of power requirements.
- Their emission levels are far below the permissible limits.

#### **Methanol-Oxygen Fuel cell**

In this fuel cell, CH<sub>3</sub>OH is used as a fuel and O<sub>2</sub> as oxidant to generate electrical energy.

**Construction:** It consists of anodic and cathodic compartments.

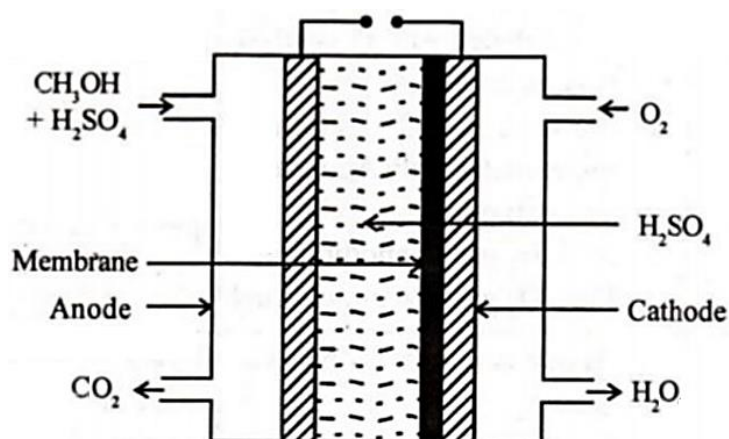
**Anode:** Made up of platinum. Methanol along with 3.7 M sulphuric acid is continuously supplied into anodic compartment as a fuel.

**Cathode:** Made up of platinum. Oxygen gas is circulated into cathodic compartment as an oxidant.

**Electrolyte:** 3.7 M H<sub>2</sub>SO<sub>4</sub>.

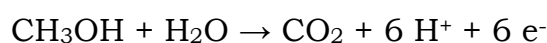


A membrane is placed adjacent to cathode to prevent the diffusion of methanol to cathode.

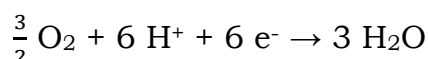


### Working:

At anode methanol undergoes oxidation to form carbon dioxide.



At cathode,  $\text{O}_2$  gets reduced in presence of  $\text{H}^+$  ions.



The net fuel cell reaction is  $\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$

Fuel and air are fed to the electrodes. The cell potential is 1.21 V.

### Advantages:

- Methanol is easily available and is very cheap.
- It contains easily oxidizable hydroxyl group and is highly soluble in  $\text{H}_2\text{SO}_4$ .
- Easy to store methanol compared to hydrogen gas.
- High efficiency of energy conversion up to 70-82%.
- No vibration, no noise, and no smoke.
- They are eco-friendly batteries.
- High power density.
- Quick operation.
- No recharge.

### Disadvantages:

- Expensive.
- Methanol is toxic.
- Lifetime is not known accurately.

### Applications:

- In all kinds of portable, automotive, and mobile applications like powering laptop, computers, cellular phones, and digital cameras.
- Fuel cell vehicles.
- Spacecraft applications.
- Any consumables which require long lasting power compared to Li-ion batteries.