UNIT-III: ENERGY - SOURCES, CONVERSION AND STORAGE

Syllabus

Energy - Sources, Conversion and Storage **11 hours**

Chemical fuels - Introduction, Calorific value - definition, gross and net calorific values; Determination of calorific value of a solid / liquid fuel using Bomb calorimeter and numerical problems on calorific value; Petroleum cracking - fluidized bed catalytic cracking; Octane number; Reformation of petrol; synthetic petrol – Fischer-Tropsch‟s process, power alcohol, biodiesel and Hydrogen as a fuel - advantages, production and storage.

Solar cells - Production of solar grade silicon, physical and chemical properties of silicon relevant to photovoltaics, doping of silicon, Construction and working of Si based PV cell, advantages.

Batteries - Basic concepts, Classification of batteries - primary and secondary batteries; Battery characteristics; Modern batteries - construction, working and applications of zinc-air, nickel-metal hydride and Li-ion batteries ($LiCoO_2$ battery).

Fuel cells - Introduction, Construction and working of methanol-oxygen fuel cell with acid electrolyte.

Self study: Power alcohol; Biodiesel

Chemical Fuels

Definition: Chemical 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.

Example: Wood, charcoal, kerosene, petrol, diesel etc.

Combustion reaction of a fuel can be represented as follows:

$$C_nH_{2n+2} + O_2 \longrightarrow CO_{2\,(g)} + H_2O_{(g)} + \text{heat}$$

- As most of the fuels contain carbon or carbon and hydrogen, the combustion involves the oxidation of carbon to carbon dioxide and hydrogen to water.
- Sulphur, if present, is oxidized to sulphur dioxide while the mineral matter forms the ash.

Classification of fuels:

- Chemical fuels are classified as primary and secondary fuels.
  A. Natural or primary fuels: They are found in nature as such. Eg: wood, peat, coal, petroleum
  B. Artificial or secondary fuels: They are prepared from the primary fuels Eg: charcoal, coke, kerosene oil, petrol etc.
- Chemical fuels are further classified as
  A. Liquid fuels
  B. Gaseous fuels

Physical state	**Primary fuels**	**Secondary fuels**
Solid	Wood, coal	Charcoal, coke
Liquid	Petroleum	Petrol, diesel, kerosene
Gas	Natural gas	LPG

Importance of hydrocarbons as fuels:

- Petroleum, coal and natural gas are excellent hydrocarbons.
- These fuels are important sources of energy in daily life.
- Hydrocarbons are used as energy sources in cooking, lighting, automobiles, production of electricity in thermal power plants etc.
- These hydrocarbon fuels meet 80% of the world's energy demand. Thus, hydrocarbons are important sources of energy.

Characteristics of a good/ ideal fuel:

1. It should possess high calorific value.
2. It should have moderate ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.
3. It should not produce poisonous products during combustion. In other words, it should not cause pollution on combustion.
4. It should have moderate rate of combustion.
5. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
6. It should not leave behind much ash on combustion.
7. It should be easily available in plenty.
8. It should have low moisture content.
9. It should be cheap.
10. It should be easy to handle and transport.

Calorific value:

Definition: It is defined as the total amount of heat liberated when a unit mass or volume of fuel is burnt completely in air or oxygen.

Gross (High) calorific value (GCV or HCV)

Definition: The total amount of heat liberated when a unit quantity of fuel is burnt completely in air and the products of combustion are cooled to room temperature. It is also called as higher calorific value (HCV).

Net (low) Calorific value (NCV or LCV)

Definition: It is the amount of liberated when a unit quantity of a fuel is burnt completely in air or oxygen and the products of combustion are allowed to escape.

Why GCV value is higher than NCV?

- In case of GCV, on cooling the combustion products, steam gets condensed to water and liberates its latent heat.
- The measured GCV includes the latent heat of steam. Therefore, it is always higher than the net calorific value.
- Whereas in case of NCV, the products of combustion are let off in to the atmosphere, the calorific value does not include the latent heat of steam.
- Therefore, NCV is always lower than GCV.

Two main reactions that occur during combustion are:

- Carbon and hydrogen present in the fuel are converted in to carbon dioxide and steam respectively, on combustion.

$$C + O_2 \longrightarrow CO_2$$

$$H_2 + 1/2\,O_2 \longrightarrow H_2O_{(liquid)} \longrightarrow H_2O_{(vapour)}$$

GCV is total heat liberated by fuel including heat of condensation of water and NCV is heat liberated by combustion of fuel excluding heat of condensation of water. Both are related by,

NCV = GCV - heat associated with steam

Calculation of Heat associated with steam

NCV = GCV – heat associated with steam

Heat associated with steam = Mass of H2O formed in combustion x Latent heat of H2O

Mass of H_2O formed in combustion = 9 x Mass of H_2 present

(1 part by mass of hydrogen produces 9 parts by mass of water)

Mass of H_2 present= $\frac{\text{\% of Hydrogen present in fuel}}{100}$ = 0.01 x % of hydrogen present in fuel

∴ Mass of H2O formed in combustion = 9 x 0.01 x % of hydrogen present in fuel

= 0.09 x % of hydrogen present in fuel

Heat associated with steam = 0.09 x % of hydrogen present in fuel x Latent heat of H2O

Latent heat of steam = 587 cal/g

∴NCV= [GCV- 0.09 x % of H_2 X 587] cal/g

OR

NCV= [GCV- 0.09 x % of H_2 X 2454] KJ/Kg

1 Cal = 4.186 J

Note: The unit of latent heat of water and unit of GCV, NCV should be same.

<u>S. I. unit of calorific value</u>: For solids, calorific value is expressed in KJ kg^{-1} (KiloJoules per kg). For gaseous fuels it is expressed in J m^{-3} (Joules / m^3).

Specific heat: Specific heat of water is the amount of heat energy required to increase the temperature of one kg of water by one degree C.

Units: J/kg/°C.

Latent heat of steam: Latent heat of steam is the amount of heat energy required to convert 1 Kg of liquid to vapor or steam

Units:K J/kg.

<u>Determination of Calorific Value</u>

The calorific value of solid and non-volatile liquid fuels is determined by bomb calorimeter.

Principle: A known mass of a solid/liquid fuel is burnt in excess oxygen. The surrounding water in the calorimeter absorbs the heat liberated. Thus, the heat liberated by the fuel is equal to the heat absorbed by the water in the calorimeter. By recording the rise in temperature of water and knowing specific heat of water, calorific value is calculated.

Construction & working: The bomb calorimeter consists of a stainless-steel vessel with an airtight lid. This vessel is called bomb. The bomb has an inlet valve for providing oxygen atmosphere inside the bomb and an electrical ignition coil for starting of combustion of fuel. The bomb is placed in an insulated copper calorimeter. The calorimeter has a mechanical stirrer for dissipation of heat and a thermometer for reading the temperature.

A known mass of the solid fuel is placed in a crucible. The crucible is placed inside the bomb. The lid is closed tightly. The bomb is placed inside a copper calorimeter. A known mass of water is taken in the calorimeter. The bomb is filled with oxygen at a pressure of 25-30 atm. The temperature t_1 in the thermometer is noted.

On passing an electric current through the ignition coil, the fuel gets ignited. The fuel burns liberating heat. The water is continuously stirred using the stirrer. The maximum temperature attained by the water, t_2 , is noted.

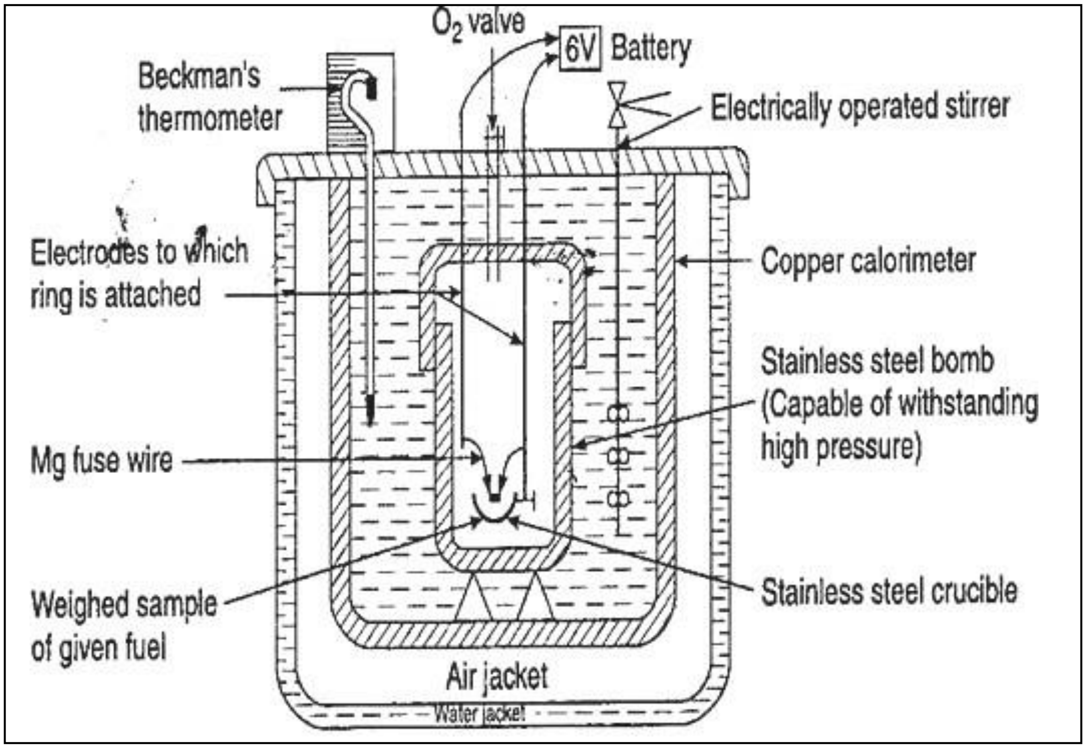


Figure 1: SCHEMATIC REPRESENTATION OF BOMB CALORIMETER

Observations and calculations:

$$\boxed{\mathrm{GCV} = \frac{(W_1 + W_2) \times S \times (t_2 - t_1)}{m}\ \mathrm{KJ/Kg}}$$

Where,

W_1 = mass of water in the calorimeter, in kg

W_2= water equivalent of the calorimeter, in kg

s = specific heat of water, in J $kg^{-1}\ {}^{o}C^{-1}$

$\Delta t = t_2 - t_1$ = rise in temperature, in ^{o}C

m = mass of the fuel, in kg

and NCV can be calculated by

NCV = GCV – 0.09 x %H x Latent Heat of steam (J/Kg)

$$\boxed{\mathrm{NCV} = \mathrm{GCV} - (0.09 \times \%H \times 587 \times 4.186)\ \mathrm{kJ/kg}}$$

$$\boxed{\mathbf{NCV = GCV - (0.09 \times \%H \times 2457)}\ \mathrm{kJ/kg}}$$

Supporting Info:

Water equivalent is nothing but the amount of water that would absorb the same amount of heat as the calorimeter per degree temperature increase.

[Numerical problems based on GCV and NCV: Refer your class notes]

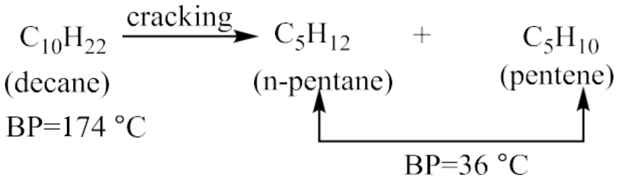
Chemical processing of crude petroleum

Processing of crude oil into desired products involve three main steps:

1. Fractional distillation
2. Cracking of petroleum
3. Reforming of petrol

CRACKING OF PETROLEUM

Definition: The decomposition of bigger hydrocarbons into simpler, low boiling hydrocarbons of low molecular weight.



$$C_{10}H_{22} \xrightarrow{\text{cracking}} C_5H_{12} + C_5H_{10}$$

What is the need for cracking?

Cracking is very important in the petroleum industry for following reasons:

1. To produce extra petrol: Heavy fractions in less demand can be cracked to produce extra petrol.
2. To improve the quality of 'straight-run' gasoline. It has to be properly blended. It is important to note that the characteristics of gasoline obtained by cracking are far more superior to the straight run gasoline.
3. To produce alkenes: Cracking always produces alkenes that van be used to many useful organic chemicals.
4. There is surplus of heavier petroleum fractions.

There are two methods for cracking:

1. Thermal cracking: The heavy oils are subjected to high temperature and pressure; when the bigger hydrocarbon molecules break down to give smaller molecules.
2. Catalytic cracking: the cracking procedure involves a suitable catalyst like aluminium silicate, $Al_2(SiO_3)_3$ or alumina, Al_2O_3

Fluidized-bed catalytic cracking (Moving-bed catalytic cracking):

Reaction conditions

Feed stock: Heavy oil

Catalyst used: y-type zeolite activated with a rare-earth oxide (12.5% Al_2O_3 + 87.5% SiO_2)

Temperature: 450-550 ^{0}C

Pressure: 1 atm

Yield: 70-80%

- The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which is circulated in gas stream.
- The vapors of heavy oil mixed with fluidized catalyst are forced up in to large reactor bed in which cracking of the heavier into lighter molecules occurs.
- Near the top of the reactor, there is a centrifugal separator called **cyclone**, which allows only the cracked oil vapors to pass on to the fractionating column, retains the catalyst in the reactor itself.
- Spent catalyst from the cracking chamber is continuously transported into the regeneration chamber through an air stream.
- The carbon deposited on catalyst particles is burnt off in **regeneration chamber**. The regenerated catalyst is transported back in to the cracking chamber together with feed stock.

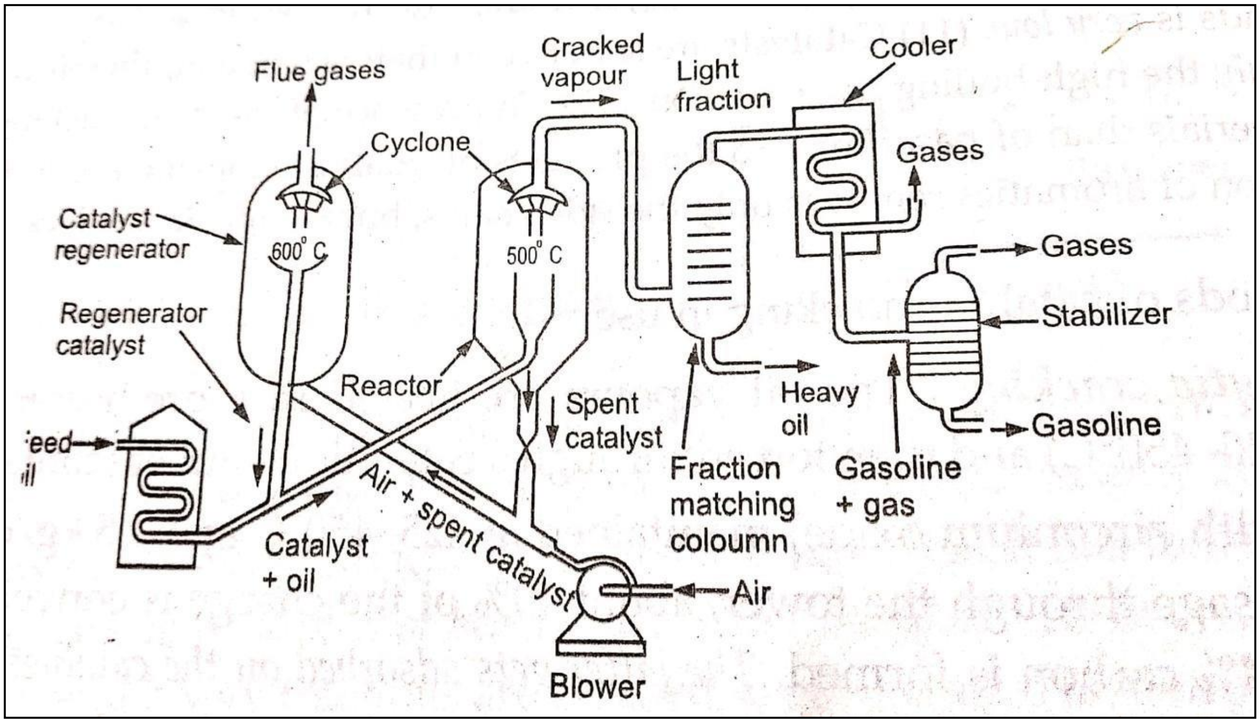


Figure 2: Fluidized-bed catalytic cracking

Advantages of fluidized-bed catalytic cracking:

1. The yield of petrol is higher.
2. The quality of petrol produced is better.
3. Fuel after cracking has higher percentage of branched chain.
4. Fuel after cracking has higher percentage of aromatics.
5. Highly controlled process.
6. No wastage of catalyst.

Disadvantages of fluidized-bed catalytic cracking:

1. Rapid mixing of fuel and catalyst may lead to non uniform residence time.
2. Agglomeration of fine particles.
3. Fine particles of catalyst may be carried away during pressurized flow.
4. Erosion of pipes.

KNOCKING IN PETROL ENGINE

- It is defined as the metallic sound similar to rattling of hammer produced in internal combustion engine due to immature ignition of fuel air mixture.
- The ratio of initial volume (volume at suction stroke) to final volume (volume at compression stroke) is called compression ratio.
- The efficiency of internal combustion engine depends on the compression ratio. "*Higher the compression ratio greater is the efficiency of the engine*"

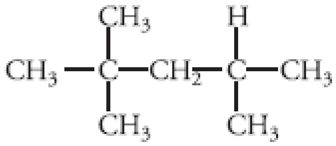
$$\text{compression ratio} = \frac{\text{volume at the end of suction stroke}}{\text{volume at the end of compression stroke}}$$

The tendency of knocking has the following trend

Straight chain paraffins > branched-chain paraffins > olefins > cycloparaffins > cyclo-paraffins > aromatics

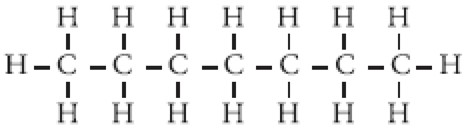
OCTANE NUMBER

Octane number of a fuel is defined as the percentage of isooctane in a mixture of isooctane and n-heptane, which has the same knocking characteristics as that of the fuel under examination, under same set of conditions.



$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

Isooctane
2,2,4-trimethylpentane
(Octane number 100)



$H-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-H$

n-heptane
(Octane number 0)

- It is observed that n-heptane knocks very badly; hence, it was arbitrarily assigned an antiknock value of zero.
- On the other hand, isooctane (2,2,4-trimethylpentane) has a high resistance to knocking and hence was arbitrarily assigned a value of 100.
- The octane number changes with the change in the structure of the hydrocarbons as follows

Straight chain alkanes < branched chain alkanes < alkenes < cycloalkanes < aromatics

REFORMATION OF PETROL

Definition of reformation of petrol: Conversion of straight chain hydrocarbons in petrol into branched chain, cyclic and aromatic hydrocarbons, resulting in up gradation of quality of the petrol is known as reformation.

How reformation improves the quality of petrol?

The octane number for straight chain hydrocarbons is low. For branched chain, cyclic and aromatic hydrocarbons, the octane number is high. Thus reformation converts the low octane number petrol into high octane number petrol.

Reformation reaction conditions:

The reaction conditions

Feed stocks: pre-processed gasoline

Catalyst: Platinum supported on alumino-silica.

Temperature: 460-530 ^{0}C

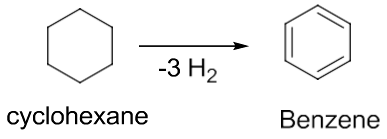
Pressure: 35-50 atm.

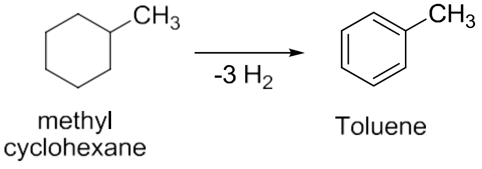
Reformation reactions:

The main reformation reactions are:

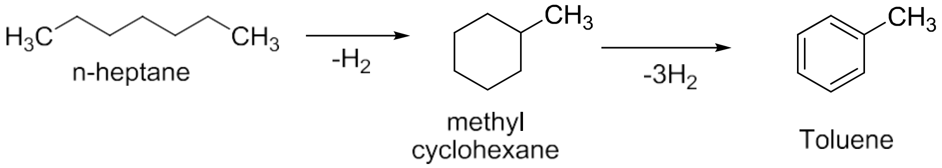
1. Dehydrogenation
2. Dehydrocyclization
3. Hydrocracking
4. Isomerization

1. Dehydrogenation





2. Dehydrocyclization



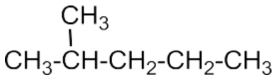
3. Hydrocracking

$$CH_3\text{-}(CH_2)_8\text{-}CH_3 \xrightarrow{Pt,\ H_2} 2\ CH_3\text{-}(CH_2)_3\text{-}CH_3$$

n-decane n-pentane

4. Isomerisation

$$CH_3\text{-}(CH_2)_4\text{-}CH_3 \longrightarrow$$



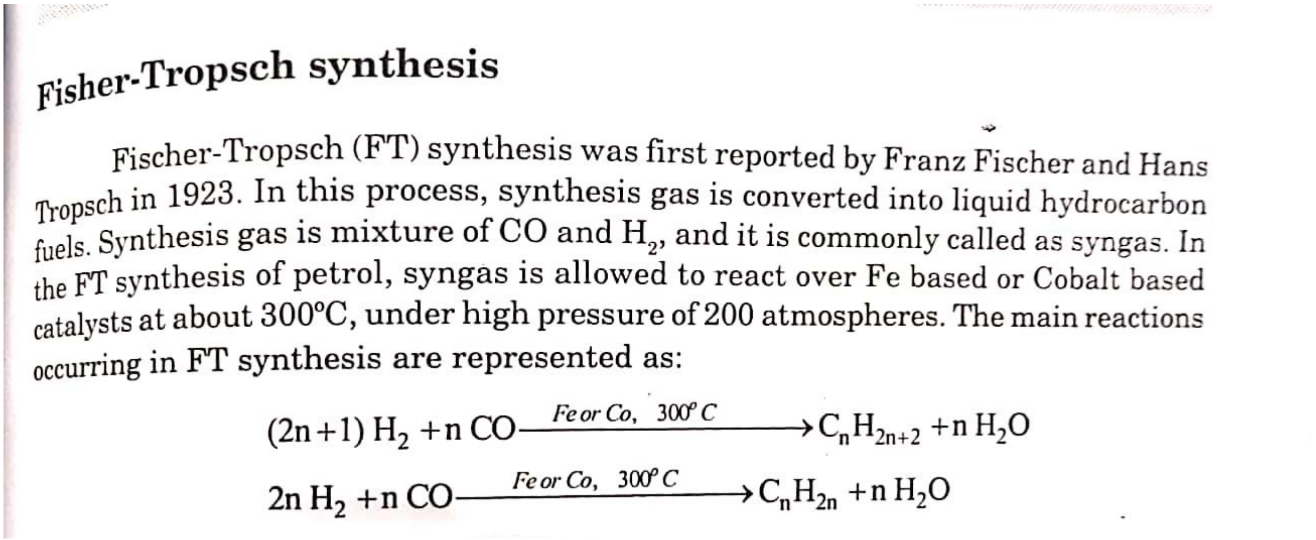
$$CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

<u>Disadvantages of non-renewable energy</u>

1. Once a non renewable energy source is used up it cannot be replaced again.
2. Non renewable energy source are highly polluting sources and increase the greenhouse gases.
3. The exposure to non renewable energy sources has increased the level of pollution.
4. The rise in temperature due to greenhouse gas accumulation.

Synthetic Petrol:

Petrol synthesized from non-petroleum carbon resources like coal, natural gase etc is called as synthetic petrol.



Fisher-Tropsch synthesis

Fischer-Tropsch (FT) synthesis was first reported by Franz Fischer and Hans Tropsch in 1923. In this process, synthesis gas is converted into liquid hydrocarbon fuels. Synthesis gas is mixture of CO and H_2, and it is commonly called as syngas. In the FT synthesis of petrol, syngas is allowed to react over Fe based or Cobalt based catalysts at about 300°C, under high pressure of 200 atmospheres. The main reactions occurring in FT synthesis are represented as:

$$(2n+1)\,H_2 + n\,CO \xrightarrow{Fe\ or\ Co,\ 300^{o}C} C_nH_{2n+2} + n\,H_2O$$

$$2n\,H_2 + n\,CO \xrightarrow{Fe\ or\ Co,\ 300^{o}C} C_nH_{2n} + n\,H_2O$$

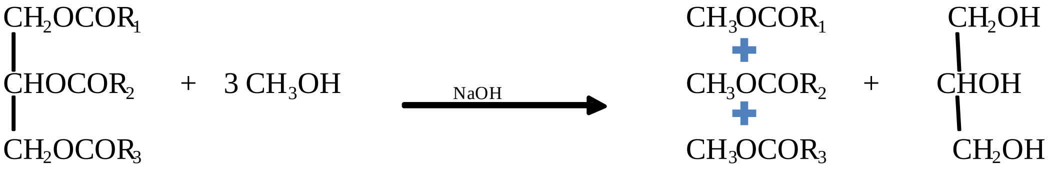
The product obtained is a mixture of hydrocarbons containing gasoline, diesel fuel, jet fuels and other chemicals. This mixture is subjected to fractional distillation to obtain petrol fraction.

Biodiesel

Biodiesel refers to a vegetable oil - or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, soybean oil) animal fat with an alcohol producing fatty acid esters.

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petrodiesel in any proportions. Biodiesel blends can also be used as heating oil.

Synthesis: Bio-diesel is commonly produced by the trans-esterification of vegetable or animal fat. The process involves reacting vegetable oils or animal fats catalytically with short chain aliphatic alcohols.



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + 3\,CH_3OH \xrightarrow{NaOH} \begin{array}{c} CH_3OCOR_1 \\ + \\ CH_3OCOR_2 \\ + \\ CH_3OCOR_3 \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Triglycerides Biodiesel Glycerol

Advantages of biodiesel fuel

- Biodiesel fuel is a renewable energy source unlike petroleum-based diesel.
- An excessive production of soybeans in the world makes it an economic way to utilize this surplus for manufacturing the Biodiesel fuel.
- It is less polluting than petroleum diesel.
- The lack of sulfur in 100% biodiesel extends the life of catalytic converters.
- The lubricating property of the biodiesel may lengthen the lifetime of engines.

Disadvantages of biodiesel fuel

- Biodiesel fuel is more expensive than petroleum diesel fuel.
- As Biodiesel cleans the dirt from the engine, this dirt can then get collected in the fuel filter, thus clogging it. So, filters have to be changed after the first several hours of biodiesel use.
- Biodiesel fuel distribution infrastructure needs improvement, which is another of the biodiesel fuel disadvantages.

HYDROGEN AS A FUEL

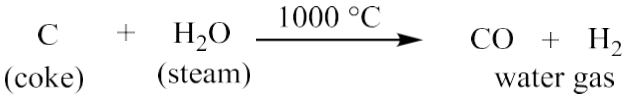
- Hydrogen is the first element of the periodic table with the electronic configuration $1s^1$.
- It is the simplest and the most plentiful element in the universe. It is always combined with other elements.
- Hydrogen fuel is a zero-emission fuel which uses electrochemical cells or combustion in internal engines, to power vehicles and electric devices.
- It is also used in the propulsion of spacecraft and can potentially be mass-produced and commercialized for passenger vehicles and aircraft.
- In a flame of pure hydrogen gas, burning in air, the hydrogen (H_2) reacts with oxygen (O_2) to form water (H_2O) and releases heat.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$$

Industrial Method of Preparation of Hydrogen

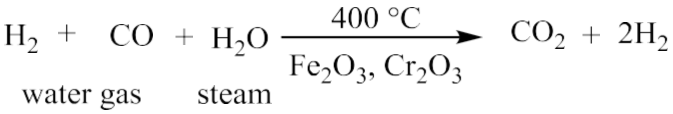
On a large scale, hydrogen gas can be prepared by the following methods.

1. By passing steam over red-hot coke: When steam is passed over red-hot coke at 1000 °C, a mixture of carbon monoxide and hydrogen (water gas) is formed.



$$\underset{\text{(coke)}}{C} + \underset{\text{(steam)}}{H_2O} \xrightarrow{1000\,°C} \underbrace{CO + H_2}_{\text{water gas}}$$

- Pure hydrogen cannot be obtained from water gas, as it is difficult to remove CO. Carbon monoxide can be removed either by
- Liquefying it at low temperature and under pressure
- Mixing the gaseous mixture (water gas with more steam and passing it over a mixture of ferric oxide (Fe_2O_3) and chromium oxide (Cr_2O_3) at 400 °C. This is called Bosch process.



$$\underbrace{H_2 + CO}_{\text{water gas}} + \underset{\text{steam}}{H_2O} \xrightarrow[Fe_2O_3,\ Cr_2O_3]{400\,°C} CO_2 + 2H_2$$

Carbon dioxide is removed by dissolving in water under pressure (25 atm) or by reacting with K_2CO_3 solution forming $KHCO_3$ and pure hydrogen gas.

2. *Steam-reforming process:* Hydrocarbons such as methane are mixed with steam and passed over a nickel catalyst at 800–900 °C.

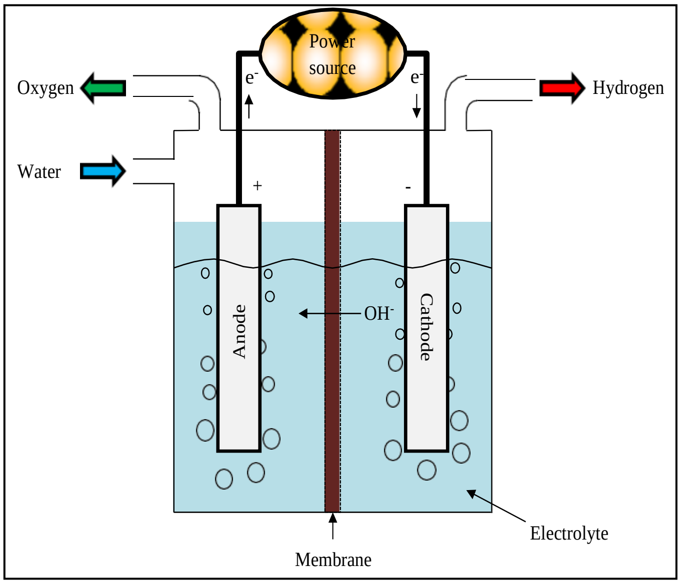
$$CH_4 + H_2O \xrightarrow[\text{Ni catalyst}]{800\text{-}900\ ^\circ C} CO + 3H_2$$

The gas emerging from the reformer is a mixture of CO, CO_2, H_2 and excess of steam. To obtain pure hydrogen, this mixture is mixed with more steam in the presence of iron/copper catalyst at 400 °C.

3. *Electrolysis of water:* Hydrogen gas of high purity can be prepared by the electrolysis of water in the presence of small amount of acid or base. During this entire energy process would create no net emissions. In this case, we would be talking about “green hydrogen”.

$$2H_2O_{(l)} \xrightarrow{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

A membrane prevents the product gases H_2 and O_2 from mixing but allows the passage of OH^- ions. Hydrogen gets collected at the cathode and oxygen is liberated at the anode.



Storage of Hydrogen

Hydrogen has high calorific value (three times greater than gasoline) but it is highly flammable and forms an explosive mixture with air; hence, its storage and transportation is one of the most challenging tasks.

The methods employed for the storage of hydrogen are as follows:

1. Physical storage:

A. Hydrogen is compressed to its liquid state at high pressure in high-pressure tanks.

B. Hydrogen can be cooled to –253 °C at a pressure of 6–350 bars to give cryogenic hydrogen.

C. Many molecules reversibly adsorb hydrogen in their structure.

The commonly used substances for hydrogen storage are as follows

- Carbon nanotubes and carbon bucky balls store hydrogen in the spaces in between and inside.
- Carbon materials such as graphene store hydrogen easily and release it on heating up to 450 °C.
- Another class of synthetic porous materials that adsorb and store hydrogen is metal– organic frameworks (MOFs). Hydrogen gas is stored in the spaces between these molecules and can be recovered for further use by raising the temperature.

2. Chemical storage:

- *As hydrides* in chemical storage, hydrogen is stored as hydrides.
- The most commonly used substance for chemical storage of hydrogen is sodium aluminium hydride, which is an inorganic compound with the formula $NaAlH_4$.
- It serves as an important agent for the reversible storage of hydrogen. Hydrogen is stored by reacting with sodium and aluminium at high pressure and temperature of about 200 °C in the presence of triethylaluminium catalyst.

$$Na + Al + H_2 \xrightarrow[200\ °C]{\text{Triethylaluminium}} NaAlH_4$$

– When heated to above 200 °C, sodium tetrahydroaluminate releases about 7.4% hydrogen by weight. Other metal hydrides used to store hydrogen are MgH_2, $LiAlH_4$, LiH, $TiFeH_2$, palladium hydride, ammonia borane, etc.

Advantages

- It is readily available.
- It doesn't produce harmful emissions.
- It is environmentally friendly
- It can be used as fuel in rockets.
- It is fuel efficient. It is renewable.

Limitations/Disadvantages

- It is expensive.
- It is difficult to store.
- It is highly flammable.

SOLAR ENERGY

Introduction

- Solar energy is a renewable energy and it inexhaustible. The earth is receiving approximately 1.8×10^{11} MW of energy which is thousands times larger than the requirement of energy for present consumption.
- Thus solar energy is the only energy that fulfils all our present and future energy needs if we utilize properly.

Utilization and conversion of solar energy:

Solar energy utilization can be of two types:

1. **Direct solar power:** It involves only one step transformation into useful forms.
    - Sunlight hits photovoltaic cell generating electricity.
    - Sunlight hits the dark absorber surface of solar thermal collector and warm the surface. This heat energy is carried by a fluid circuit.
2. **Indirect solar power:** It involves multi step transformation into useful forms.
    - Photosynthesis
    - Photocatalysis

Photovoltaic Cell

Solar photovoltaic cell is a device used to convert solar light directly in to an electric current.

Principle: PV cells rely on the photoelectric effect i. e., ability of certain elements to emit electrons when electromagnetic radiation of sufficient energy falls on it. The photons possess certain amount of energy as evident from Planck quantum equation.

$$E = h\,\frac{c}{\lambda}$$

where, h is Planck's constant, c is velocity of light and λ is the wavelength of the radiation.

Construction: A typical silicon solar cell consists of n-type material (phosphorus doped silicon) and a p-type (boron doped silicon) material made of silicon. In the fabrication of device, these n-type and p-type materials are joined to form a p-n junction. On top of n-type connecting front electrodes are placed. The metal back contact is attached to p-type layer. An antireflective coating is filled in between the front electrodes to avoid the reflection of sunlight. Finally p-type and n-type layers are joined externally to the circuit. The complete solar cells are sealed to avoid the environmental contact.

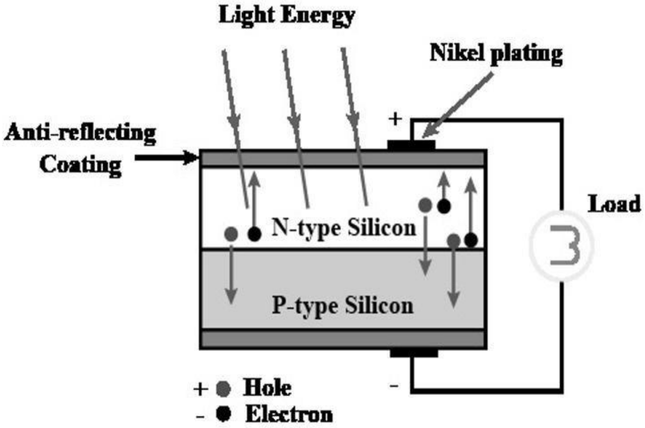


Figure 3: Typical representation of solar cells

Working: When sunlight is incident on solar cells photon strikes on p-n junction. Then electron hole pair will be created at the junction by the absorption of photon. This electron hole pair diffuses towards respective layer based on affinity. The electrons diffuse towards n-type later and holes are diffused towards p-type layer. These layers are connected externally through a circuit, hence current will be generated.

Advantages of Solar Cells

- Solar cell is renewable energy which can be continuously drawn from the sun.
- It is economic friendly energy because once it installed there will be minimum maintenance charges for small usage.
- Solar energy is environment friendly and green energy because it doesn't produce any greenhouse gasses and no pollutants.
- It doesn't involve any combustion reaction or radioactive residue hence no pollution.

Disadvantages of Solar Cells

- Space utilization: Solar cells required large area for installation.
- It requires high investment cost for a big power plant.
- During the rainy season power production is less hence grid maintenance will be difficult.
- Solar energy is produced only in the day time hence storage will be a big challenge.

NUMERICAL PROBLEMS

1. A coal sample with 93% carbon, 5% of Hydrogen and 2% Ash is subjected to combustion in a bomb calorimeter. Calculate GCV and NCV.

Given that
Mass of the coal sample = 0.95g
Mass of water in copper calorimeter = 2000g.
Water equivalent wt of calorimeter = 700g.
Rise in temp = 2.8^0C
Latent heat of = 587 cal/g.
Specific heat of water = 1 cal/g/0C

$$GCV = \frac{(W+w) \times S \times \Delta t}{m}$$

$$= \frac{(2000+700) \times 10^{-3} \times 2.8^0C \times 4.184}{0.95 \times 10^{-3}\ kg}$$

$$= 33295.83\ J/kg.$$

$$NCV = GCV - 0.09 \times \%H2 \times 587 \times 4.184\ J/kg.$$

$$= 33295.83\ J/kg - 0.09 \times 5 \times 587 \times 4.184\ J/kg.$$

$$= 32190.62\ J/kg$$

2.When 0.84g of coal was burnt completely in Bomb calorimeter the increase in temp of 2655 grams of water was 1.85^0C if the water equivalent calorimeter is 156g Calculate GCV.

$$GCV = \frac{(W+w) \times S \times \Delta t}{m}$$

$$\frac{(2655+156) \times 1.85 \times 10\text{-}3 \times 4.187}{0.84 \times 10^{-3}}$$

$$25921.26\ J/Kg$$

3. Calculate GCV and NCV of a fuel from the following data.Mass of fuel=0.75g, W=350g. t $=3.02^0C$, Mass of water = 1150,% H_2=2.8.

$$GCV = \frac{(W+w) \times \Delta t \times S}{m}$$

$$= \frac{(1150+350) \text{ x}10^{-3}\text{x } 3.02 \text{ x } 4.184}{0.75 \text{ x } 10^{-3}}$$

$$\text{GCV} = 25271.\ 36 \text{ KJ/Kg}$$

$$\text{NCV} = \text{GCV} - 0.09 \text{ x H x } 587 \text{ x } 4.184$$

$$= 25271.36 - 0.09 \text{ x } 2.8 \text{ x } 587 \text{ x } 4.184$$

$$\text{NCV} = 24652.44 \text{ KJ/Kg}$$

4. Calculate GCV of a fuel sample of a coal form the following data. Mass of the coal is 0.6g. Water equivalent wt of calorimeter is 2200g. Specific value 4.187 Kg/KJ/C rise in temperature = 6.52^0C.

$$\text{GCV} = \frac{(\text{W1}+\text{W2}) \text{ x S x } \Delta t}{m}$$

$$= \frac{(2200) \text{ x } 10^{-3} \text{ x } 4.184 \text{ x } 6.52}{0.6 \text{ x } 10^{-3}}$$

$$= 100025.49 \text{ KJ/Kg.}$$

BATTERIES:

BATTERIES

Galvanic cell: Galvanic cell is a device for converting chemical energy into electrical energy through a spontaneous redox reaction.

Battery: A battery is an electrochemical device which consists of two or more galvanic cells connected in series or parallel or both which produces electricity by means of redox chemical reactions.

Basic components of battery

The basic components in a battery are **anode**, **cathode**, **electrolyte** and **separator**

1. ***Anode:*** The electro-active material at anode is oxidized and liberates electrons to the external circuit.

   $$M \longrightarrow M^{n+} + ne$$

   The anode electro active material should have:

   - Ease of oxidation (i. e., low reduction potential)
   - Capacity to deliver high Columbic output.
   - Good conductivity
   - High stability
   - Ease of fabrication

2. ***Cathode:*** The electro-active material at anode is reduced and accepts electrons from the external circuit.

   $$M^{n+} + ne \longrightarrow M$$

   The cathode electro active materials should have:

  - High reduction potential
  - High resistant to the electrolyte

3. ***Electrolyte:*** It provides medium for transfer of ions between the anode and cathode. It is commonly a solution (or slurry) of an acid, alkali or salts having good ionic conductivity.

   It should be:

   - Safe to handle
   - Non-reactive with the electrode
   - Safe to handle

4. ***Separator:*** It is used to separate anode and cathode compartments to prevent internal short circuiting. It is an electrical insulator.

   Eg: Cellulose, cellophane, nafion membranes etc.

Classification of batteries:

1. Primary batteries: These are non-rechargeable batteries.

   Eg: Zn-MnO_2 battery, Li-MnO_2 battery etc.

2. Secondary batteries: These are rechargeable batteries.

   Eg: Nickel-cadmium battery, Lithium-ion battery etc

3. Reserve batteries: In these batteries, one of the active components (e.g. electrolyte) of the battery is separated from the rest of the components. It is assembled just before the use. Eg: Mg-AgCl and Mg-CuCl batteries; both can be activated by adding water.

Working of a battery:

Discharging: During discharge, oxidation takes place at the anode and reduction takes place at the cathode. The reactions are spontaneous. Chemical energy is converted into electrical energy. It acts as a galvanic cell during discharge.

At anode: $M \longrightarrow M^{n+} + ne$

At cathode: $M^{n+} + ne \longrightarrow M$

Charging: During charging, reverse reactions take place. The reverse reactions are non-spontaneous reactions. The battery is connected to an external d.c. power supply. Electrical energy is converted in to chemical energy. During charging it acts as a electrolytic cell.

At anode: $M^{n+} + ne \longrightarrow M$

At cathode: $M \longrightarrow M^{n+} + ne$

Characteristics of Batteries:

1. Voltage:

- The voltage of a battery mainly depends upon the emf of the cells which constitute the battery system which is given by Nernst equation,

$$E = E^0_{cell} - \frac{2.303RT}{nF} \log K$$

Where, $E^0_{cell} = E^0_{cathode} - E^0_{anode}$ and K is the reaction quotient which is the ratio of the product of molar concentration of the reaction product molecules to that of reactants.

The maximum voltage can be derived when:

- The difference in the electrode potentials of cathode and anode is high.
- Polarization and over potential must be minimum.
- The internal resistance of the cell must be low.

2. Current:

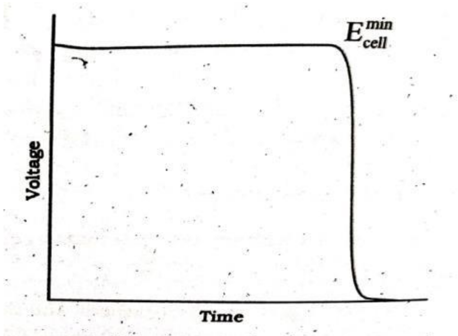
- Current is a measure of the rate at which the battery is discharging.
- Higher the rate of spontaneous reaction, higher is the current.
- Higher the surface area of the electrodes, higher is the rate of reaction. Current is measured in A.

3. Capacity:

- Capacity is a measure of the amount of electricity that may be obtained from the battery. It is expressed in Ah (ampere hours).
- The charge (C) in Coulombs is given by the Faraday's relation:

$$C = \frac{w \times n \times F}{M}$$

where w is the weight of active material present at one of the electrodes, n = number of electrons involved in discharge reaction, F = 96500 C/mol, and M its molar mass. “More is the length of the flat portion of the curve, better is the capacity of the battery”.



Voltage against time for fixed current discharge

4. Energy density:

- It is the ratio of energy available from the battery to its weight (or volume). It may be expressed in Wh/kg.
- If a battery can be discharged at a current I and at an average voltage E for a period of time t, then the energy density is given by

$$\text{Energy density} = (I \times E \times t) / w$$

where w is the weight of the battery.

5. Power density:

- It is the power per unit weight (or volume) of the battery.
- If a battery can be discharged at a current I and at a voltage E, then the power density is given by

$$\text{Power density} = (I \times E)/w$$

where w is the weight of the battery. It may be expressed in W/kg.

6. Energy efficiency: The energy efficiency of a rechargeable battery is given by

$$\%\text{ of Energy efficiency} = \frac{\text{Energy released during discharge}}{\text{Energy required for charging}} \times 100$$

7. Cycle life: It is the number of discharge–charge cycles possible in a rechargeable battery before failure occurs. A good battery must have high cycle life.

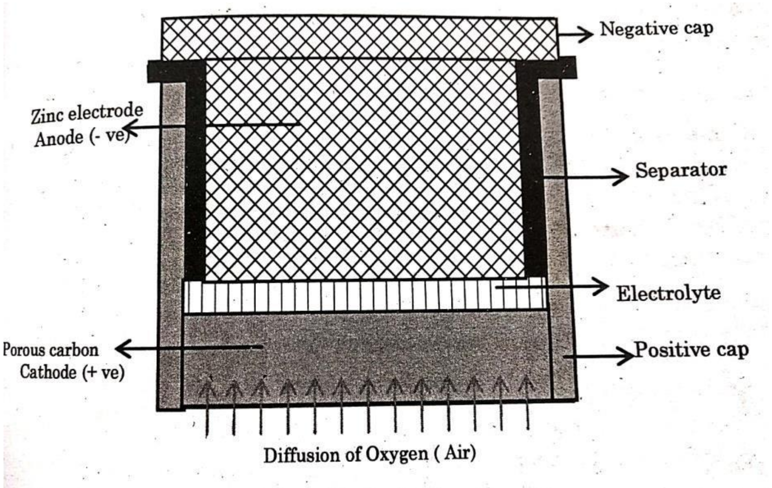
8. Shelf life: The duration of storage of a battery, at the end of which the battery is able to give required performance is called shelf life. A good battery must have long shelf life.

9. Tolerance to service conditions: The battery must be sufficient for the intended application. This means that it must be able to produce the right current with the right voltage. It must have sufficient capacity, energy and power. It should also not exceed the requirements of the application by too much, since this is likely to result in unnecessary cost; it must give sufficient performance for the lowest possible price.

MODERN BATTERIES

Zinc-air battery

- Zinc-air battery is an metal-air battery.
- Major advantage of this battery is an active material at cathode is O_2 from the air. This reduces the weight of the battery and **increases the capacity and energy density**.



Zinc-Air button cell

Cell representation: *Zn/NaOH/Air,C*

Construction:

Anode: Loose, granulated powder of zinc of high purity.

Cathode: Carbon blended with Mn oxide catalyst.

Electrolyte: Highly conductive solution of KOH in water with a gelling agent.

Separator: Nylon

Cell reactions:

Anode: $2\,Zn + 4\,OH^- \longrightarrow 2\,ZnO + 2\,H_2O + 4\,e^-$
Cathode: $O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$
Overall reaction: $2\,Zn + O_2 \longrightarrow 2\,ZnO$

Applications:

- Zinc air batteries are primarily designed to provide power to behind-the-ear, and in-the-ear miniature hearing aids.
- Pagers, remote communications, railways and military applications.

Nickel-Metal hydride battery:

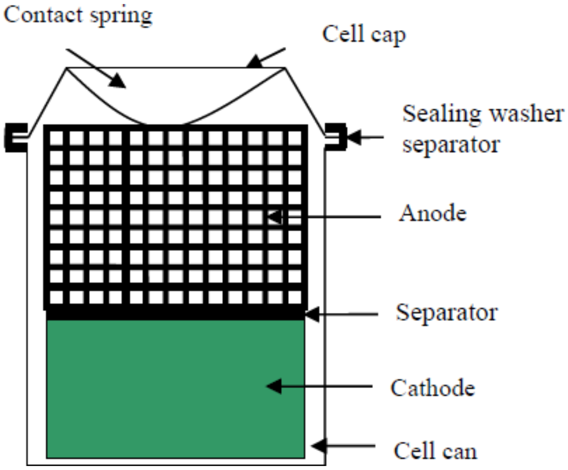
Construction:

Anode: Porous nickel grid pasted with metal hydride (such as TiH_2, VH_2, or ZrH_2) and a hydrogen storage alloy (such as $LaNi_5$ or $TiNi_2$).

Cathode: Nickel hydroxide, $Ni(OH)_2$.

Electrolyte: An aqueous solution of KOH.

Separator: Polypropylene membrane



Cell representation: MH, M/KOH(28%)/Ni(O)(OH), $Ni(OH)_2$

Cell reactions:

$$\text{Anode: } MH_2 + 2\,OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M + 2\,H_2O + 2\,e^-$$

$$\text{Cathode: } 2\,NiO(OH) + 2\,H_2O + 2\,e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,Ni\,(OH)_2 + 2\,OH^-$$

$$\text{Overall reaction: } MH_2 + 2\,NiO(OH) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M + 2\,Ni\,(OH)_2$$

Applications:

- Cellular phones, laptop computers, electric vehicles and spacecrafts.

Lithium-ion battery:

Principle:

- Li-ion batteries are secondary batteries.
- During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery.
- The Li-ion is transfers between anode and cathode through an Electrolyte.

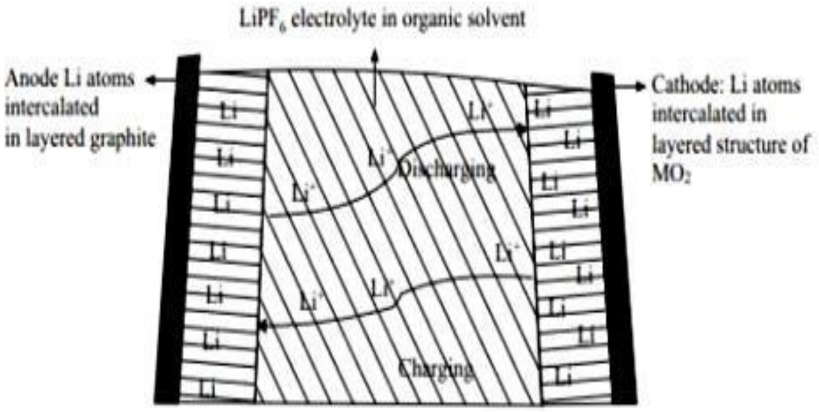
Construction:

Anode: Lithiated Graphite carbon

Cathode: Lithium cobalt oxide ($LiCoO_2$)

Separator: Polypropylene membrane

Electrolyte: Lithium salt in an organic solvent ($LiPF_6$ in ethylene carbonate).



Cell representation: *Li/Li⁺,C/LiPF₆ in ethylene carbonate/Li-CoO₂*

Working:

- The traditional batteries are based on galvanic action but Lithium ion secondary 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.

Cell reactions:

At Anode: During discharging of battery, Lithium atoms present in graphite layer (one Li atom present in every 6C atoms) are oxidized, liberating electrons and lithium ions. Electrons flow through the external circuit to cathode and lithium ions flow through the electrolyte towards cathode.

At Cathode: Cobalt is reduced and lithium atoms and are inserted into the layered structure of CoO_2. The lithium ion is inserted and exerted into the lattice structure of anode and cathode during charging and discharging.

During discharge current flows through external circuit and light glows. During charging, no electrons flow in the opposite direction.

$$\text{Anode: } LiC_6 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} C_6 + Li^+ + e^-$$

$$\text{Cathode: } CoO_2 + Li^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} LiCoO_2$$

$$\text{Overall reaction: } LiC_6 + CoO_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} C_6 + LiCoO_2$$

Advantages:

- They have high energy density than other rechargeable batteries.
- They are less weight.
- They produce high voltage out about 3.7 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.

FUEL CELLS

Definition: Fuel cell can be defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.

– Compared to conventional combination (combustion) of fuel and oxidant in IC engines or thermal power plants, conversion efficiency is high because no loss of energy in different steps (heat to mechanical to electrical) and no harmful by products.

Components:

Fuel: Hydrogen, methanol, ethanol etc

Oxidant: air/oxygen, hydrogen peroxide

Electrolyte: acid (sulphuric acid/ phosphoric acid), base (KOH)

Anode and cathode catalyst (generally noble metal based)

Working:

Fuel is fed into the anodic compartment where it undergoes oxidation; oxidant is fed into the cathodic compartment where it gets reduced. Protons/hydroxyl ions cross over the separator and electrons flow in the external circuit generating current

Reactions:

At anode: Fuel $\longrightarrow$ Oxidized product + n electrons

At cathode: Oxidant + n electrons $\longrightarrow$ Reduced product

Net reaction: Fuel + oxidant $\longrightarrow$ oxidized product + reduced product

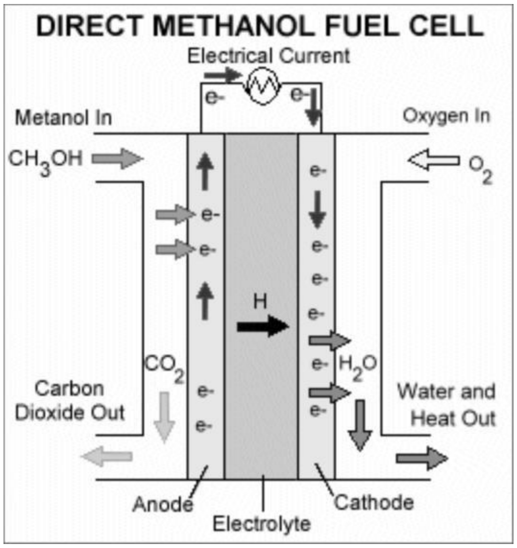
Methanol-oxygen fuel cells

In this, methanol is used as the fuel and oxygen gas is used as an oxidant. It consists of porous nickel sheets impregnated with electro-catalysts. Pt/Ru catalyst is deposited on anode and platinum on cathode. Sulphuric acid is used as an electrolyte. A solid ion exchange membrane (fluorinated sulphonic acid membrane) which is a good conductor for proton is used as separator. The reactions are shown in equations:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H+ + 6e-$

Cathode: $3/2\ O_2 + 6H+ + 6e- \rightarrow 3H_2O$

Overall: $CH_3OH(l) + 3/2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$



Advantages of fuel cells:

1. Theoretically, the efficiency can be 100%. In practice, the efficiency is 50-80% which is high compared to conventional methods.
2. Harmful products are absent. Hence fuel cells are environment friendly.
3. No need of charging.
4. Silent operation.
5. No moving parts. Hence wear and tear is eliminated.

Disadvantages: catalysts are expensive, separator is expensive, poisoning of the catalyst by carbon monoxide intermediate

Note:

1. KOH is not used as electrolyte as it reacts with CO_2 and gets converted to K_2CO_3. Thus the conductivity of the electrolyte decreases as well as efficiency.
2. The advantage of using acid electrolyte is that the CO_2, a product of the reaction can be easily removed.

FUEL CELLS	BATTERIES
Do not store chemical energy	Stores chemical energy
Reactants are supplied continuously	Reactants are within the cell
Need expensive noble catalysts	Not required
No charging is required	Charging is required in secondary batteries
Never become dead	Limited span in use
Useful for long-term services for electricity generation	Useful as portable power