Physics

Energy Studies - II

M. Sc. (Sem. - IV) (PHOT - 244 (H4) (Paper-IV)

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Energy Studies - II

(PHOT-244H4)

M. Sc. (Sem. - IV) (Paper-IV)

(According to New Syllabus of Savitribai Phule Pune University from June 2021)

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M.Sc. (Sem. - III) (Paper IV)
Physics (Energy Studies – I) (PHOT-234H4)

UNIT 3

Hydrogen Energy

3.1 Introduction :

Hydrogen holds to potential to provide clean, reliable and affordable energy supply that can enhance economy, environment and security. It is flexible and can be used by all sectors of economy. It is non-toxic and recyclable. Due to these qualities it is considered to be an ideal energy carrier in the projected future. Hydrogen can be produce by variety of energy sources, such as solar, nuclear and fossil fuels and can be converted to useful energy forms efficiently and without detrimental environmental effects. When burn as fuel or converted into electricity it joins with the oxygen to produce energy with water as the only emission. Despite these benefits, realization of hydrogen economy faces multiple challenges. Unlike gasoline and natural gas, hydrogen has no existing, large scale supporting infrastructure. Building of such large infrastructure requires major investment. Although hydrogen production, storage and delivery techniques are currently in commercial use by chemical and refining industries, existing hydrogen storage and conversion technologies are too costly for widespread use in energy applications.

3.2 Hydrogen Fuel :

3.2.1 Importance of Hydrogen as a Future Fuel :

The major advantages for the use of hydrogen as a future fuel are listed below

1) **Hydrogen is the simplest, lightest and abundant element in the universe:** It is made up of one proton and one electron. It is recognized by English Chemist and Physicist Henry Cavendish in 1766 and named by Antoine Lavoisier, a Frenchman

in 1783. Its density is 1/14th that of air and 1/9th that of natural gas. About 90 % of atoms in the universe are Hydrogen.

2) Reduce depletion of fossil fuels:

In last two hundred years, we have consumed 60 % of fossil fuels (coal, oil and natural gas). Even today 85 % of raw energy comes from the fossil sources. These reserves are continuously diminishing and are becoming increasingly expensive and will not exist for future generation.

3) To reduce greenhouse gas emissions:

Due to excessive use of fossil fuels such as coal, oil, natural gas, propane and wood burn, pollutants like CO, CO2, a variety of hydrocarbons and quantities of particulate matters are produced. It is found that the environment have an adverse effect on it. The climate has changed. Global mean temperature has risen by 1°F and is expected to increase to 3.6 °F by 2100, the sea level has risen by 4-10" and is expected to increase 20" by 2100. The precipitation over land has increased by 1 % and its intensity is likely to increase by 2100. On the other hand pure hydrogen produces only heat energy, water and trace amounts of oxides of nitrogen when burned. Oxides of nitrogen and water are natural in earth's atmosphere. Thus, hydrogen is totally non- polluting.

4) Hydrogen is among the safest of all fuels:

Hydrogen is as safe as gasoline, diesel or natural gas. Other fuels take longer to disperse or may spill onto the ground. Some, like gasoline, require specialized cleanup efforts and present toxic hazards to the nearby environment. Hydrogen is 14 times lighter than air and 9 times lighter than gasoline. In the event of an accidental release, it disperses rapidly upward in the atmosphere. Hydrogen is among the safest of all fuels because it is lightest compared to other fuels.

5) To have energy security of a nation:

Fossil fuels particularly crude oil is confined to few areas of the world i.e. Middle East. This region is susceptible to disturbances and consequent disruptions of crude oil supply. The continuous supply of crude oil is governed by political, economic and ecological factors. These factors act together. The high fuel prizes, while at the same time environmental policies are demanding reduction in greenhouse gases and toxic emission. Thus it is necessary to promote use of divers, domestic and sustainable energy resources.

6) To have a coherent energy strategy:

A coherent energy strategy is required addressing demand taking into account the whole energy life cycle including fuel production, transmission and distribution network, energy conversion and impact on energy equipment manufactures and the end user of energy system.

7) **Hydrogen is economically competitive with the gasoline or diesel:**
Under the hood of today's automobiles, IC engines capture only 15-20 % of the energy in vehicles. By harnessing the fuel's energy via an electro-chemical reaction rather than a thermo-chemical (combustion) reaction, a fuel cell can convert 40-65 % of hydrogen's energy into electricity to propel a car. Fuel cells running on pure H2 are more efficient.

8) **Hydrogen is also an excellent energy carrier:**
The standard heating value of hydrogen gas is 12.2 MJ/m^3 compared with average 38.3 MJ/m^3 for natural gas. The heating value of liquid hydrogen gas is 8400 MJ/m^3 compared with 44 MJ/m^3 for gasoline (jet fuel). Therefore, hydrogen is an excellent energy carrier.

3.2.2 Sources of Hydrogen :

Hydrogen can produce from conventional as well as non-conventional energy sources. (See figure 3.1)

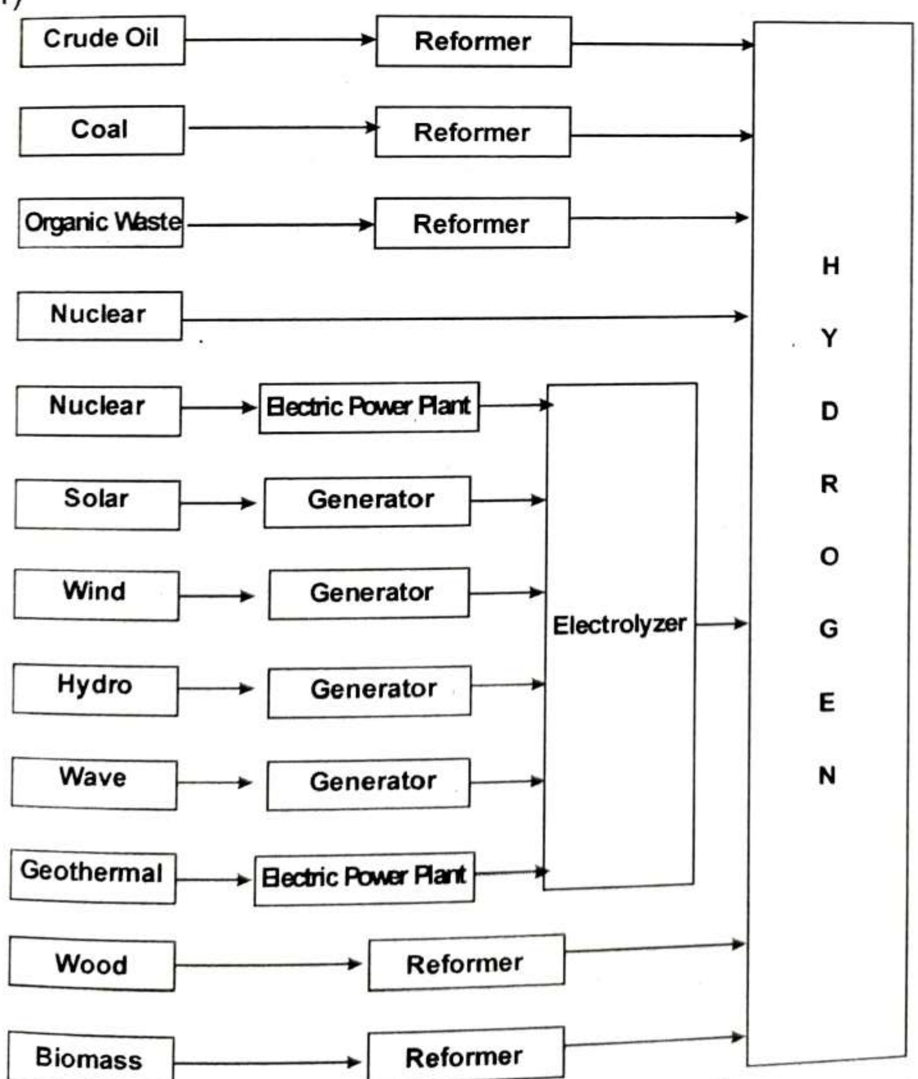

Fig. 3.1 : Hydrogen Production Pathway

3.2.3 Fuel of Vehicles :

You may be familiar with the terms gasoline, LPG, CNG, and others. These are the fuels that will enable you to finish your lengthy drive. The best performance of your car is ensured by using the right oil as fuel. This article will provide all the information you need to know about the fuel that is best for your vehicle.

1) Petrol :

Petrol, also known as gasoline, is one of the most common fuel types for a vehicle. It is transparent and is derived via the fractional distillation of petroleum. It is used in spark-ignited combustion engines and is available in multiple variants. Let's take a look at its pros and cons-

Pros:

- It is cost-effective.
- Provides optimum acceleration.
- Petrol stations are easily available.
- Suitable for all types of ranges.

Cons:

- This fuel emits a high level of toxic gases.
- It offers lower mileage than diesel.

Ideal for:

4-wheeler private cars, bikes

Price per litre:

It is important to remember that the cost of gasoline differs in each state. Here is the table comprising the respective petrol prices in different Indian cities.

Indian Cities	Petrol Price Per Litre as on 1 March, 2023
Delhi	Rs.96.72
Mumbai	Rs.106.25
Bengaluru	Rs.101.96
Kolkata	Rs.105.97
Chennai	Rs.102.58
Surat	Rs.96.31
Chandigarh	Rs.96.19

2) Diesel :

Despite the current scenario, diesel consumption witnessed recovery with a 27% rise. This speaks volumes about the popularity of this fuel. Like petrol, diesel is also obtained from the fractional distillation of petroleum oil that is specially tailored for a diesel engine.

Pros:

- Offers value-for-money and is efficient for long travels.
- Features high torque and delivers excellent performance on express lane.
- It offers enhanced acceleration.

Cons:

- Diesel engines require high maintenance and hence incur whopping expenses.
- A diesel engine does not cater to every make and model.

Ideal for:

Trucks, trains, public buses

Price per litre:

Like petrol, diesel prices differ in each state. Here is a table for your reference.

Indian Cities	Diesel Price Per Litre as on 1 March, 2023
Delhi	Rs.89.62
Mumbai	Rs.94.22
Bengaluru	Rs.87.91
Kolkata	Rs.92.71
Chennai	Rs.94.19
Surat	Rs.92.06
Chandigarh	Rs.84.26

3) **Compressed Natural Gas (CNG) :**

CNG or Compressed Natural Gas comprises compressed methane less than 1% by volume. It is one of the emerging fuel types for a car in urban areas with the primary objective to reduce pollution.

Pros:

- It is free from lead and sulphur and is popularly known as "Green Fuel."
- Features a high auto-ignition temperature (540 degrees Celsius) and limited flammability range of 5%-15%. It implies that 5%-15% of CNG concentration in the air will not lead to accidental burning, thus, ensuring safety.
- It is safe to use as it is stored in certified cylinders, which are leak-proof. Since it is a light gas, it disperses and mixes with the air if it leaks.

Cons:

- Limited availability of CNG stations, unlike petrol or diesel stations.
- It occupies at least 1/3rd of the vehicle's boot space. This makes it difficult for a sedan or other car owners to load the luggage in the cargo space.
- A CNG's car performance deteriorates after 3 to 4 years of usage. The engine's optimum performance also decreases by 10% after regular use for one year.

- It hampers the functionality of fuel injectors, making them dry quickly. It deteriorates engine performance in the long run.
- A CNG-powered vehicle has a lower fuel economy compared to other vehicles.
- The cost of conversion from conventional petrol or diesel-powered cars to CNG is high.

Ideal for:

It is widely used in passenger cars. Models like Audi A5 2,0 TFSI CNG and BMW 3 Series (E36) can run on CNG. Besides, vans, buses, trucks and more are suitable to run on CNG.

Price per kg:

The following table illustrates the costs of CNG in 5 metropolitan cities in India.

Indian Cities	CNG Price Per Kg as on 1 March, 2023
Delhi	Rs.79.56
Mumbai	Rs.87.00
Bengaluru	Rs.87.50
Kolkata	Rs.64.69
Chennai	Rs.77.20
Surat	Rs.79.59
Chandigarh	Rs.92.25

4) Bio-Diesel :

The mixture of diesel with other oils produces bio-diesel. Converting vegetable oil, animal fat, and waste cooking oil into bio-diesel is known as transesterification. Since it constitutes natural ingredients, it is one of the best alternatives for biofuel.

Pros:

- Environment-friendly and emits 11% lower carbon monoxide compared to other fuels.
- It features lower flashpoints and burns at a higher temperature. The storage of this fuel is simple as there is a lesser risk of sudden ignition.
- It is a non-toxic and renewable source of energy and, hence, ensures sustainability.
- Helps increase the lifespan of an engine. It acts as a solvent to remove the dirt deposited in the engine and restore its optimum performance, preventing frequent wear and tear.
- Vehicle-owners can use it in diesel engines with or without any modifications.
- This fuel reduces dependency on foreign countries for oil imports.

Cons:

- It is not suitable for use in lower temperatures as it is susceptible to gelling. Gelling is a process in which a fuel's paraffin component solidifies and forms a gel-like part in colder temperatures.
- Although bio-diesel's advantages include removing dirt from the engine, this dirt gets clogged into the gasket, leading to damage. It also damages an engine's rubber houses.
- The fuel efficiency of a bio-diesel powered vehicle is lower than others. It reduces fuel efficiency by 1%-2%.
- It is more expensive than petroleum.
- Bio-diesel is made from animal fat, vegetable oil, and the like. It affects food supply and increases the prices of the given products, leading to food shortages.
- It has regional restrictions as specific crop productions are not possible in every region.

Ideal for:

Diesel-powered vehicles are fit to run on bio-diesel. Specifically manufactured trucks, vans, and SUVs are also approved to run on bio-diesel.

Price per litre:

Here are the costs of bio-diesel in each metropolitan city.

Indian Cities	Bio-diesel Price Per Litre as on 1 March, 2023
Delhi	Rs.69.44
Mumbai	Rs.69.00
Bengaluru	Rs.67.20
Kolkata	Rs.71.12
Chennai	Rs.77.00
Surat	Rs.67.00
Chandigarh	Rs.70.00

5) Liquid Petroleum Gas (LPG) :

LPG or Liquid Petroleum Gas is obtained from crude oil and natural gas. It constitutes hydrocarbon gases such as propane and butane.

Pros:

- The high octane content in Auto LPG ensures a vehicle's optimum performance.
- LPG removes the carbon and acids from the engine, extending its longevity.
- It saves up to 40% of running costs compared to petrol and is safe from spillage.
- It emits 75% less carbon monoxide than petroleum and 60% less carbon dioxide than diesel.
- The conversion cost of LPG is affordable compared to CNG.

- It features anti-knocking characteristics, facilitating a higher octane number.

Cons:

- It is heavier than air. Hence, in case of leakage, it creates a suffocating environment.
- It has 10% lower fuel efficiency than petrol.
- Storage of LPG requires heavy cylinders, which ultimately increases the weight of the engine.

Ideal for:

It is suitable for light-duty bio-fuel vehicles. Specific brands like Chevrolet and Maruti Suzuki manufacture LPG-powered cars in India.

Price per 14.2kg:

Take a look at the costs of Auto LPG in each metropolitan city –

Indian Cities	LPG Price Per 14.2 Kg as on 1 March, 2023
Delhi	Rs.1103.00
Mumbai	Rs.1102.50
Bengaluru	Rs.1105.50
Kolkata	Rs.1129.00
Chennai	Rs.1068.50
Surat	Rs.1108.50
Chandigarh	Rs.1112.50

6) **Ethanol or Methanol :**

It is alcohol with a high octane number. It is a renewable and biodegradable energy source and does not emit a significant amount of carbon dioxide and nitrogen dioxide. Presently, India uses up to 10% of ethanol-blended fuel. The Indian government is planning to increase ethanol production as petrol and diesel prices reach new heights every day.

Pros:

- It features low flammability and is safe to use.
- This fuel can be manufactured from natural gas and coal. It also increases the dependence on domestic fuels.

Cons:

- It offers low mileage and, hence, offers poor fuel economy.
- This fuel is corrosive and damages the vehicle in the long run.

Ideal for:

It is primarily used in racing cars. Also, it is mixed with gasoline in smaller quantities for use in existing on-road vehicles.

Price per litre:

The Indian Government raised the price of ethanol based on C-heavy molasses to ₹45.69 per litre. The cost of B-heavy molasses remained at ₹57.61 per litre as of 2020.

3.3 Hydrogen Production :

3.3.1 Production of Hydrogen by various methods :

There are various methods used for the production of hydrogen. These methods are discussed in detail in the following sections. Each production method has its advantages and disadvantages.

1) **Steam Methane Reforming (SMR) :**

Step I: Methane is catalytically reformed at elevated temperature and pressure. The reforming reaction is carried out in a reformer containing tubes filled with nickel under at temperatures 500°C and 950 °C and pressure around 30 atmospheres. The reforming reaction is described by:

$$CH_4 + H_2O + Heat \longrightarrow 3\,H_2 + CO$$

Step II: An excess of steam is used to enhance conversion and to prevent thermal cocking and coking using nickel catalyst reaction

$$2\,CO \longrightarrow CO_2 + C + Heat$$

Conversion of syngas gets to the desired H2 product.

$$CO + H_2O \longrightarrow CO_2 + H_2 + Heat$$

Step III: Purification process is then done by pressure swing adsorption to remove water, methane, CO2, N2 and CO and produce 99.99 % pure hydrogen. Chemical absorption of H2 can be achieved using amine contractor followed by methanation to eliminate CO and CO2 impurities.

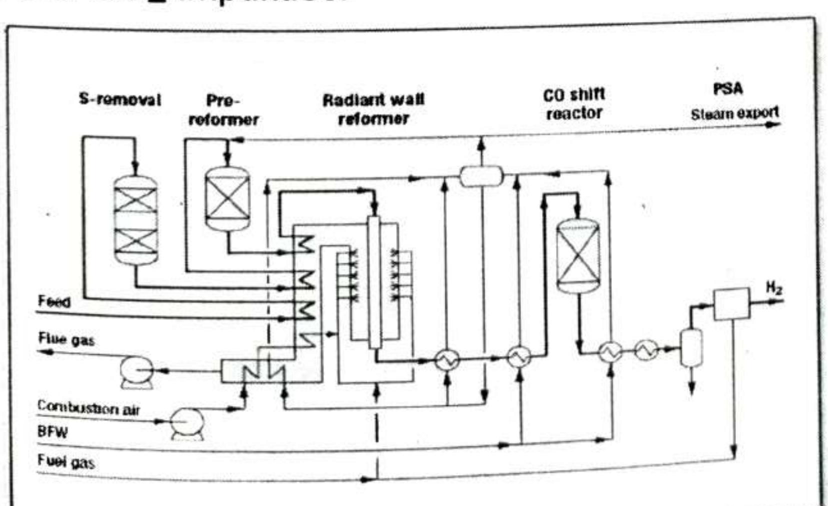

Fig. 3.2 : Steam methane reforming production of hydrogen

a) Advantages of steam methane reforming method:

Some of the major advantages are,

i) Proven technology and high efficiency (83 %)

ii) Economically favorable (H2 price ~ $ 0.75/kg)

iii) Ideal for centralized production

iv) CH4 pipelines already in place

b) Disadvantages steam methane reforming method:

These limitations are,

i) CO2 by-product

ii) Limited long-term methane supply and Subject to CH4 feed price fluctuations

2) Partial oxidation and auto-thermal reforming of methane :

Partial oxidation and auto thermal reforming of methane are similar to SMR.

a) Partial oxidation of methane :

In partial oxidation process, the methane is directly oxidized in a one-step reaction. The syngas-mixture of CO and H2 is produced via following the reaction:

$$CH_4 + \frac{1}{2} O_2 \longrightarrow CO + 2H_2 \qquad \Delta H = -36 \text{ KJ/mol}$$

The total oxidation and formation of coke during the reaction is prevented by high reaction temperature and controlled oxygen feed. The catalyst is not required, but has the potential to enhance hydrogen yield and lower the required temperature. A variety of catalysts are under investigation, including Rd, Pt, and Ni based catalysts, although research has indicated that Rd based catalysts have an advantage in requiring a higher activation energy for over- oxidation of hydrogen. The partial oxidation process requires careful control and design reactors to make possible heat exchange or dilution of reactants to prevent thermal runaway or possible explosions from the exothermic process. An oxygen plant is usually installed on site to supply pure oxygen feed. Nitrogen oxides may also be produced which require clean- up after process.

b) Auto thermal reforming of methane :

In auto thermal reforming process, the partial oxidation and the reforming reaction are combined and methane is react with a mixture of steam and oxygen catalytically. It is differs from the steam methane process of in which methane is react with steam only.

A more advanced partial oxidation process is auto thermal reforming, a hybrid of partial oxidation and SMR processes. Both, partial oxidation and reforming reactions take place inside an auto thermal reactor. The mixture of CO and H2 is produced via following total oxidation reaction.

$$CH_4 + H_2O + \text{Heat} \longrightarrow 3H_2 + CO$$

Some part of the heat from the exothermic partial oxidation reaction is supplied to the heat required for the endothermic reforming reaction between methane and steam. As some portion ofthe feed methane is burned within the reactor vessel less heat is required. Soot formation in the auto thermal process is under investigation. Manipulating the operating conditions and mapping soot formation may provide the information necessary for commercial use of auto thermal reformers. Development and testing of soot-tolerant catalysts is also underway.

c) **Advantages partial oxidation process:** Some of the major advantages are,

i) It is a proven technology

ii) It is economically reasonable (H_2 price ~ $ 1.39/kg)

iii) May be scale down for distributed production of hydrogen

iv) The methane pipelines already in place

d) **Disadvantages partial oxidation process:** Some of the major disadvantages are,

i) The CO_2 is by-product

ii) Limited long-term methane supply

iii) Subject to methane feed price fluctuations

iv) The efficiency is lower than SMR process (70-80 %)

v) Catalysts are still under development for CH_4

3) **Coal Gasification :**

The figure 3.3 shows the flow diagram of coal gasification process. Similar to the steam methane reforming, the coal gasification method of production of hydrogen involves three steps. First, the treatment of coal feedstock with high temperature steam to produce synthesis gas. Second is the catalytic shift conversion and third is the purification of hydrogen.

Step I: Treatment of coal feedstock with high temperature

The coal is chemically broken down by high temperature (1330 °C) and high-pressure steam to produce raw synthesis gas, as described by the following reaction:

$$\text{Coal (carbon source)} + H_2O \longrightarrow H_2 + CO + \text{Impurities}$$

The heat required for this gasification step comes from controlled addition of oxygen, which allows partial oxidation of small amount of coal feedstock.

Step II: Catalytic shift conversion

Syngas passes through shift reactor converting a portion of the CO to CO_2.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The syngas entering reactor is pretreated by passing through a quench cooler where it is saturated with water. The shift reactor is adiabatic, operates at a high temperature (~ 450 °C), and contains a sulfur tolerant cobalt molybdate shift catalyst. Iron/chrome oxide catalysts are also be used at pressures below 50 bars if H_2S

removal is carried out before the shift reaction. The shifted syngas contains 60 % H2 mixed with primarily CO2 and some residual CO. CH4, O2,N2 and H2S may also exist as impurities depending on the composition of the feed coal. The mixture is cooled and enters a lower temperature shift reactor, after which it is cooled again.

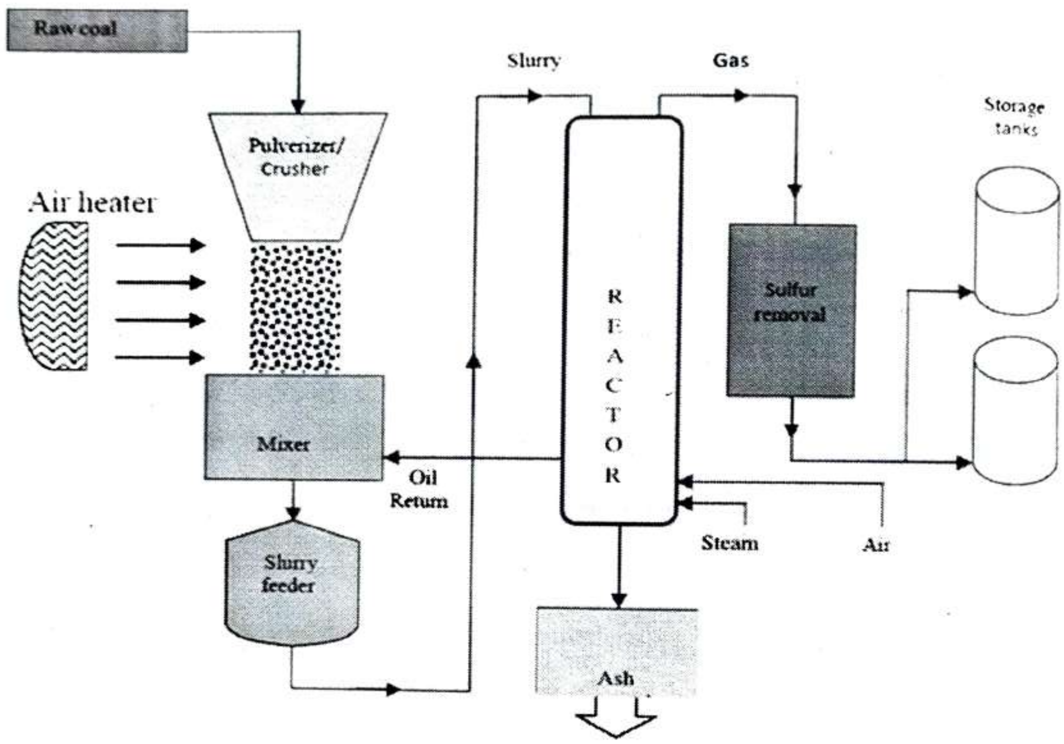

Fig. 3.3 : Flow diagram of coal gasification process

Step III: Purification of the hydrogen product

Physical absorption removes 99 % of H2S impurities. The majority of H2 in the shifted syngas (85%) is then removed as 99.999% pure H2 in a pressure swing adsorption unit (PSA). In the case of CO2 sequestration, a secondary absorption tower removes CO2 from the remaining shifted syngas. This waste gas is burn to produce electricity. A major field of application of coal gasification is in the manufacture of ammonia for fertilizer production. For this purpose in various developing countries such plants are based on hard coal and process must widely use Koppers-Totzek process.

a) Advantages coal gasification process: Some major advantages are,

i) It is a proventechnology.

ii) It is ideal for large-scale hydrogen production.

iii) The efficiency of coal gasification reforming is 63 %.

iv) Coal gasification is economical method (0.92 $/kg).

v) Abundance of coal resources in the world.

b) Disadvantages coal gasification process:

Some major disadvantages are,

i) The CO2 is by-product.

ii) The cost of production of hydrogen depends on coal feed price fluctuations.

iii) Less hydrogen rich than SMR hence low efficiency in hydrogen production.

3.3.2 Direct electrolysis of water :

The process of splitting water into H2 and O2 by means of electric current is known as electrolysis. This is the simplest method of H2 production. The figure 3.4 shows an electrolysis cell of electrolysis process. It consists of two electrodes of metal or carbon immersed in an aqueous conducting solution called electrolyte (KOH solution). A source of direct electric current is connected to the electrodes so that an electric current flows through the electrolyte from positive electrode (or anode) to negative electrode (or cathode) As a result water in the electrolyte solution decomposed into hydrogen gas which is released at cathode and oxygen gas at anode. Although only water split, an electrolyte is required because the water itself is a very poor conductor of electricity.

Under alkaline conditions, this process may be described by the reactions,

$$\text{Cathode:} \quad 2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

$$\text{Anode:} \quad 2OH^- \longrightarrow \tfrac{1}{2} O_2 + H_2O + 2e^-$$

$$\text{Net Effect:} \quad H_2O \longrightarrow H_2 + \tfrac{1}{2} O_2$$

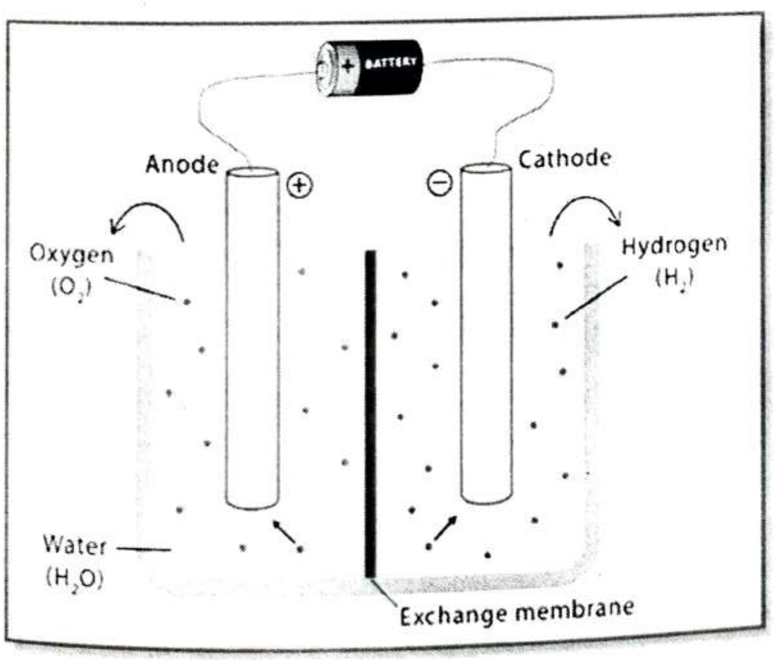

Fig. 3.4 : Electrolysis of Water

The net effect is to produce H2 and O2 by supplying only water and electricity. The theoretical voltage for this decomposition of water at atmospheric pressure and 77 °F is 1.23 V. At this voltage, reaction rates are very slow. In practice, higher voltages are applied to increase the reaction rates. However, this results in increased heat losses to the surroundings, decreasing energy efficiency. The necessary voltage may be lowered by introducing catalysts or sophisticated electrode surfaces that increase surface area. Increasing temperature and pressure may also increase the efficiency at the cost of additional material costs to resist corrosion or higher pressures.

3.3.3 Direct thermal decomposition of water :

In sulfur-iodine cycle, the heat necessary to drive three coupled thermo-chemical reactions is provided from nuclear or solar heat. The coupled reaction system takes with water as input. With a series of reactions involving sulfur and iodine, H2 and O2 are produced. The process flow-sheet for three coupled thermo-chemical reactions in sulfur iodine cycle is shown in figure 3.5.

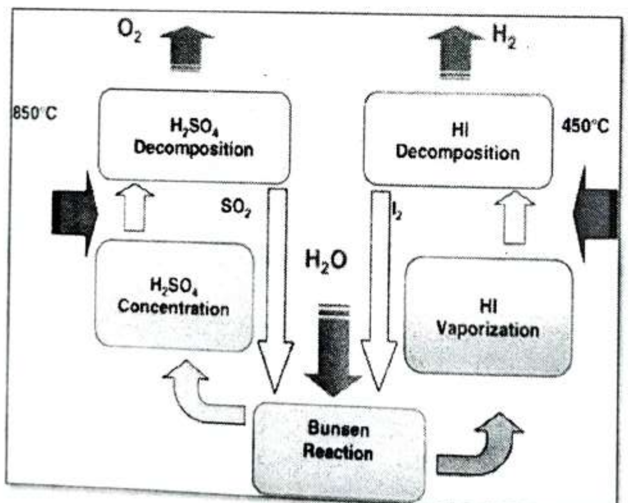

Fig. 3.5 : Sulphur-Iodine thermo-chemical cycle

In first reaction (called Bunsen reaction), excess of molten I2 reacts with SO2 and H2O to produce a two phase product with a heavier HI and lighter H2SO4 separated by gravity.

$$2\,H_2O + SO_2 + I_2 \longrightarrow H_2SO_4 + 2\,HI \qquad (< 120\ ^\circ C)$$

The second reaction is the catalytic decomposition of sulfuric acid.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + {}^1/_2\,O_2 \qquad (>800^\circ C)$$

The third reaction is decomposition of HI which, is achieved using reactive distillation. The overall effect is to produce H2 and O2 with the addition of only water and heat to the cycle, without producing any harmful emissions or by-products.

Net Effect: $H_2O \longrightarrow H_2 + \frac{1}{2} O_2$

The Calcium-Bromine cycle is under research and development.

Advantages of sulphur iodine cycle process:

Some of the major advantages are,

1) Emission free
2) Not dependent on fossil sources

Disadvantages sulphur iodine cycle process:

Some of the major disadvantages are,

1) High capital cost
2) Highly corrosive conditions
3) Safety concerns
4) Process require high temperature
5) Low efficiency (42%)
6) H2 selling price ~ 2.01 $/kg

3.3.3 Biological and biochemical methods of hydrogen production :

A) Biological Method :

In this method the ability of plants especially algae to split water during the photosynthesis process is utilized. An artificial system is devised which produce hydrogen and oxygen from water in sunlight using isolated photosynthetic membrane and other catalyst. Since this process essentially a decomposition of water using photons in presence of biological catalysts, the reaction is called photolysis of water. There is three distinct functional components couple together in the system shown in figure 3.6.

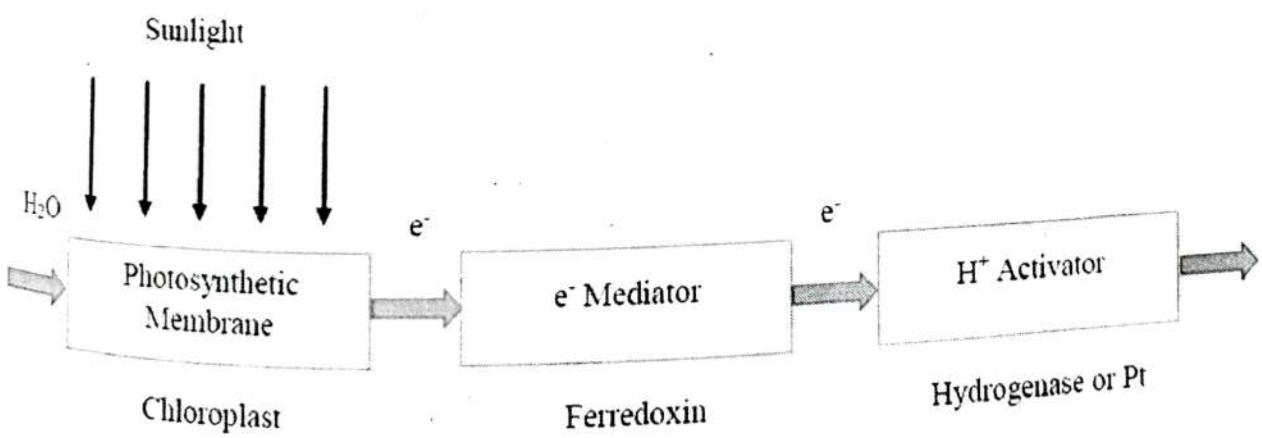

Fig. 3.6 : Principle of photo-biological hydrogen production

Photosynthetic membrane: The photosynthetic membrane absorbs light to generate oxygen, electrons and protons.

Electron mediator: An electron mediator is reducible by photo-synthetically generated electrons.

Proton activator: A proton activator accepts electrons from the reduced electron mediator and catalyzes the reaction:

$$2H^+ + 2e^- \longrightarrow H_2$$

A system with chloroplast (a small bodies containing the chlorophyll in green plants) as a photosynthetic membrane to split oxygen and hydrogen, ferredoxin as electron mediator and hydrogenase (an enzyme) or finely dispersed platinum as a proton activator, has been successfully tested.

1) Advantages of biophotolysis method:

Some of the major advantages are,

i) Renewable

ii) CO2 by-product used as a carbon source by bacteria

iii) Not dependent on fossil sources

2) Disadvantages of biophotolysis method:

Some of the major disadvantages are

i) Very low efficiency (24 %)

ii) Capacity limited by depth of light

iii) High capital cost of bio-reactor

iv) H2 selling price ~ 5.52 $/kg

B) Biochemical Method :

Biomass can be used to produce hydrogen in two ways, first is the direct gasification process and second is by pyrolysis to produce liquid bio-oil from reforming. Biomass refers to crops or other agricultural products and other plant species. It may also include municipal solid waste or sewage, a fraction of which is burned to produce steam for the process.

Direct biomass gasification process

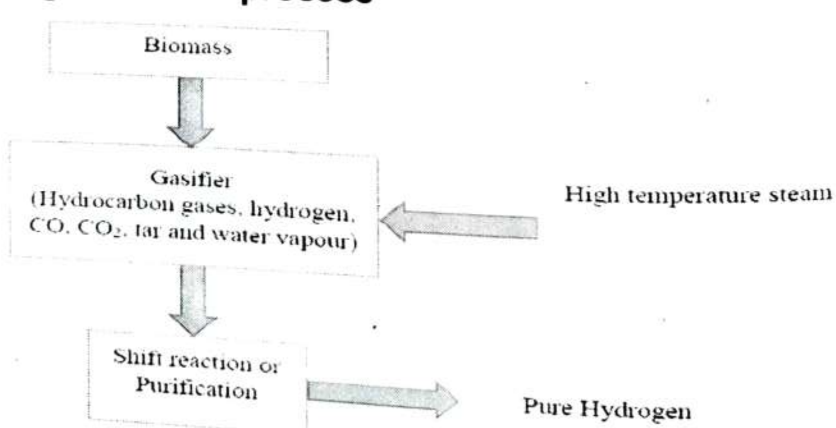

Fig. 3.7 : Schematic of direct biomass gasification process of hydrogen production

The direct biomass gasification process of production of hydrogen is a three step process. First the biomass is treated with high temperature steam in an oxygen-blown or air-blown gasifier to produce an impure syngas mixture composed of hydrocarbon gases, hydrogen, CO, CO_2, tar and water vapor, carbon residue and ash are left behind in the gasifier. Secondly, a portion of the char is gasified by reaction with oxygen, steam, and hydrogen, while another portion is combusted to provide heat. Finally the third step is followed by the shift reaction and purification.

1) **Advantages direct biomass gasification process:**

i) Renewable
ii) Independent of fossil fuels
iii) CO_2 by-product considered environmentally neutral

2) **Disadvantages direct biomass gasification process:**

i) Variation in price due to varying hydrogen content in biomass
ii) Limited by rate at which biomass is available
iii) Difficulties in transportation of biomass
iv) Low efficiency (40-50 %)
v) H_2 selling price ~ 1.21-2.42 $/kg

C) **Liquid Bio-oil Pyrolysis Process:**

In liquid bio oil pyrolysis process, first the biomass is thermally decomposed at 450-550 °C to get liquid bio-oil. It is an endothermic process. The bio-oil produced is a liquid composed of oxygenated organics and water. The bio-oil then is steam reformed using a nickel-based catalyst at 750-850 °C, followed by a shift reaction to convert CO to CO_2. The reactions are:

$$\text{Biomass} + \text{Energy} \longrightarrow \text{Bio-oil} + \text{Char} + \text{Gas Impurities} \quad \text{(pyrolysis)}$$

$$\text{Bio-oil} + H_2O \longrightarrow CO + H_2 \quad \text{(reforming)}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \text{(shift reaction)}$$

The yield of the process is limited, with a maximum of only 8.6 g H_2/100 g bio-oil. The process can be represented by the overall reaction:

$$CH_{1.9}O_{0.7} + 1.26\ H_2O \longrightarrow CO_2 + 2.21\ H_2$$

1) **Advantages liquid bio-oil pyrolysis process:**

i) Renewable
ii) Independent of fossil fuels
iii) Liquid bio-oil is more easily transportable than bulk for biomass distributed production

2) Disadvantages liquid bio-oil pyrolysis process:

i) Variation in price and yield due to varying hydrogen content in biomass

ii) Limited by rate at which biomass is available

iii) Low efficiency (56%)

iv) H2 selling price ~ 1.26-2.19$/kg

3.4 Hydrogen Storage :

In energy system there is need to store energy somewhere between the production point and utilization point. The need of energy storage due to inevitable mismatch between the production rate of energy and fluctuations in energy demand for energy by the users. Hydrogen can be stored in different ways depending on various fields of applications. There are five principle methods that have been considered for hydrogen storage. These methods are,

1) Compressed gas storage
2) Liquid storage
3) Line pack system
4) Underground storage
5) Storage in metal hydrides

1) Compressed gas storage:

On a small scale or moderate scale, H2 is frequently stored under high pressure in strong steel cylinders. This method of storage is expensive and bulky because very large quantities of steel are required. This method of H2 storage is used in industries where requirement is small. But, when H2 as a fuel is to be used this storage method is not suitable.

2) Liquid storage:

This is also called cryogenic H2 storage. A more practical approach is store H2 as a liquid at a low temperature. Liquid H2 boils at -253 ^{o}C. Thus it must be stored at this or below this temperature. Hence this type of H2 storage requires large facilities for H2 liquefaction and storage tanks. Sometimes H2 stored in vacuum, insulated storage vessels in which liquid gas is maintained in the liquid state at considerable higher temperature by using super insulation.

3) Line pack system:

The use of line pack storage in the natural gas industries provides relatively small capacity storage system but with a very fast response time that can take care of minute by minute or hour by hour variations in demand. A transmission and distribution system running on H_2 has similar potential compared with natural gas but the capacity is reduced by a factor of 3 due to reduced heating value of H_2.

4) **Underground storage:**

The cheapest way to store large amount of H2 is underground storage. The underground storage of H2 includes depleted oil and gas reservoir and aquifers. Since H2 gas can escape easily through porous materials, some geological formations which are suitable for storing the natural gas may not be suitable for storing the hydrogen gas.

5) **Storage in metal hydrides:**

A number of metals and alloys form solid compounds, called metal hydrides, by direct reaction with hydrogen gas. When the hydride is heated, the hydrogen is released and original metal or an alloy is recovered for the further use. Thus metal hydrides provide a possible means for H2 storage. An important property of the metal hydrides is that the pressure of the H2 gas released by heating a particular hydride depends mainly on temperature and the gas pressure almost remains constant until the H2 content is completely exhausted.

During the charging up with hydrogen heat is always produced at the same time and in order to withdraw the hydrogen from the hydride it is always necessary to add heat. Several studies have been made to find a metal hydride that should satisfy the requirement of hydrogen storage. These requirements include the following.

a) The metal or alloy should be inexpensive
b) Metal hydride should store large amount of hydrogen per unit volume and per unit mass.
c) The hydride should form without difficulty by reaction of the metal with hydrogen gas and should remain stable at roomtemperature.
d) Hydride should release at a significant pressure from it at a moderate temperature.

There are three promising hydrides which are generally used to store hydrogen. These hydrides are Lanthanum-Nickel (LaNi6), Iron-Titanium (FeTi) and Magnesium-Nickel (Mg2Ni).

3.5 Utilization of Hydrogen :

1) **Residential uses:**
a) Electricity for lighting and operating domestic appliances
b) Domestic cooking
c) Radiant space heaters

2) **Industrial uses:**
a) As a fuel instead of coal or coal derived gases to reduce oxide ores
b) As a chemical reducing agent

3) **Road Vehicles:**

The use of H_2 in internal combustion (IC) engines for automobiles, buses, trucks and farm machineries has attracted interest as a means of conserving petroleum products and of reducing atmospheric pollution. The advantages claimed for hydrogen fuel engines are

a) High combustion efficiency (40 % - 65 %).

b) Amount of CO2 and hydrocarbons in the exhaust will be small. However, emission of nitrogen oxide will be high due to high combustion temperature. But injecting water into the cylinder the emission level can be reduced.

4) Air craft applications:

The main advantage of use of hydrogen in air craft is its overall low weight of fuel and storage tank than for ordinary fuel jet. Because of lower weight it is possible to archive shorter take off run, stepper climbing paths and smaller engine thrust (less noise production).

5) Electric power generation using fuel cells

3.5.1 Fuel cell – Principle, Construction and Applications :

A fuel cell is an electrochemical energy conversion device that continuously converts chemical energy of a fuel directly into electrical energy. Continuous operation requires supply of fuel and oxidant and removal of water vapor, spent fuel, spent oxidant, inert residue and heat, etc. It is known as a cell because of some similarities with a primary cell. Like a conventional primary cell it also has two electrodes and an electrolyte between them and produces dc power. It is also a static power conversion device. However, active materials are generally supplied from outside unlike conventional cell where it is contained inside the cell. Fuel is supplied at the negative electrode, also known as fuel electrode or anode and oxidant is supplied at positive electrode, also known as oxidant electrode or cathode. Main exhaust of a fuel cell if pure hydrogen is used as fuel (and pure oxygen as oxidant), is water vapor, which is not a pollutant. In case of hydrocarbon fuel, carbon dioxide is also produced. If air is used as oxidant, nitrogen (spent air) is also produced in the exhaust. No other pollutant such as particulate matter, NO_x and SO_x are produced. Some amount of heat is also produced, which can be easily dissipated to the atmosphere or used locally for heating purpose. No cooling water is required, unlike conventional thermal power conversion devices where substantial quantity of cooling water is required. As conversion of chemical energy of fuel to electrical energy occurs directly without intermediate thermal stage, the efficiency of conversion is better and not limited by Carnot efficiency of thermal storage. The efficiency of a practical fuel cell may be around 50%. The average cell voltage is typically about 0.7 V (on rated load) and several cells may be connected in series to increase the voltage. The current depends on the electrode area and can be increased by connecting several cells in parallel. Thus, modules of different sizes can be constructed by series-parallel connection of required number of cells.

Classification of Fuel Cells:

Fuel cells can be classified in several ways.

Based on the type of electrolyte:

1) Phosphoric Acid Fuel Cell (P AFC)
2) Alkaline Fuel Cell (AFC)
3) Polymer Electrolytic Membrane Fuel Cell (PEMFC) or Solid Polymer Fuel Cell (SPFC) or Proton Exchange Membrane Fuel Cell (PEMFC)
4) Molten Carbonate Fuel Cell (MCFC)

Based on the types of the fuel and oxidant:

1) Hydrogen (pure)-0xygen (pure) fuel cell
2) Hydrogen rich gas-air fuel cell
3) Hydrazine-Oxygen/hydrogen peroxide fuel cell
4) Ammonia-air fuel cell
5) Synthesis gas-air fuel cell
6) Hydrocarbon (gas)-air fuel cell
7) Hydrocarbon (liquid)-air fuel cell

Based on operating temperature:

1) Low temperature fuel cell (below 150°C)
2) Medium temperature fuel cell (150-250°C)
3) High temperature fuel cell (250-800°C)
4) Very high temperature fuel cell (800-1100 ^{0}C)

Based on application:

1) Fuel cell for space applications
2) Fuel cell for vehicle propulsion
3) Fuel cell for submarines
4) Fuel cell for defense applications
5) Fuel cell for commercial applications

Based on the chemical nature of electrolyte:

1) Acidic electrolyte type
2) Alkaline electrolyte type
3) Neutral electrolyte type

Solid Oxide Fuel Cell (SOFC) :

Certain solid oxides (ceramics) at high temperature can be used as electrolyte. For example, zirconium oxide containing a small amount of other oxide to stabilize the crystal structure has been used as an electrolyte. The material is able to conduct O- - ions at high temperature. The negative electrode is made of porous nickel and positive electrode employs metal oxide, e.g. indium oxide. The operating temperature is in the range of 600-1000° C. Due to high temperature operation, catalyst is not required. These cells could utilize same fuels as used in MCFC. At the fuel electrode H2 and CO react with O- - ions present in the electrolyte to produce H2O and CO2. The two electrons released (per ion) flow through external path to constitute load current. Like MCFC, the heat of discharge can be utilized as process heat or for additional power generation using steam plant. The output voltage at full load is about 0.63 V. A tubular construction of SOFC is shown in figure 3.8.

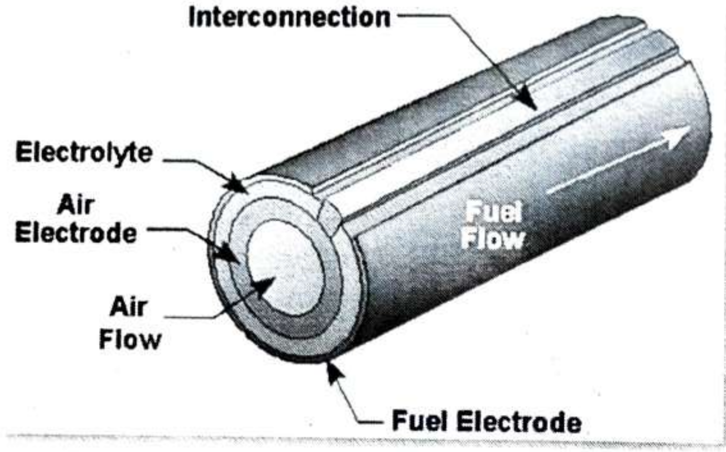

Figure 3.8 Solid Oxide Fuel Cell (SOFC)

The reactions at the electrodes are:

At positive electrode: $H_2 + O^{--} \longrightarrow H_2O + 2\,e^-$

$CO + O^{--} \longrightarrow CO_2 + 2\,e^-$

At negative electrode: $O_2 + 4\,e^- \longrightarrow 2\,O^{--}$

The overall reaction is: $H_2 + CO + O_2 \longrightarrow H_2O + CO_2$

Advantages of Fuel Cell :

1) It is quiet in operation as it is a static device.
2) It is less pollutant.
3) Its conversion efficiency is more due to direct single stage energy conversion.
4) Fuel cell plant can be installed near point of use, thus transmission and distribution losses are avoided.
5) No cooling water is needed as required in condenser of a conventional steam plant. The heat generated can be easily removed and discharged to the atmosphere or used locally.
6) Because of modular nature, any voltage current level can be realized and the capacity can be added later on as the demand grows.
7) Fuel cell plants are compact and require less space.
8) Availability of choice from large number of possible fuels.
9) Can be used efficiently at part load from 50-100%, and
10) No charging is required.

Potential Applications of Fuel Cell :

1) Fuel cells can be effectively used for load leveling. When the generation exceeds the demand, excess generated energy can used to convert and store hydrogen by electrolysis. During peak load time, when demand exceeds generation, the stored hydrogen can be used in fuel cells to meet additional demand.
2) A central station power plant using fuel cell is also possible using gasified coal as fuel.
   The efficiency of such a plant would be higher due direct energy conversion as compared to conventional thermal plant. Thus, coal will be used more efficiently with reduced emissions.
3) Fuel cells are also suited for dispersed generation. By locating the fuel cells near load center, transmission and distribution cost would avoided/ reduced, although there would be some cost for transportation the hydrogen.
4) To meet the demand of isolated sites such as construction sites, military camps and small village community or hamlet, fuel cells are more suited than diesel generator set.
5) For remote and unreachable locations fuel cell can be used unattended for a long period.
6) Emergency/auxiliary supply to critical loads such as hospitals, etc. can be better met using fuel cells as compared to diesel generator set.
7) Fuel cells can also be used as a mobile power source in vehicles, submarines, spacecrafts, etc. Hydrogen-oxygen, alkali fuel cell has been used successfully to provide electric power in Apollo and shuttle spacecrafts in USA.
8) Fuel cells are also proposed as a power source for propulsion of electric vehicles.
9) Fuel cells can be used to power portable electronic devices (e. g. mobile phones and other low power appliances, especially those used in military) as substitute for primary or rechargeable batteries. Instead of waiting for several hours for recharging, small cartridge of methanol can be replaced in the same way as an ink cartridge in a computer printer.

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Review Questions

Q. 1. Give the importance of hydrogen as a fuel. What are the sources from which we can produce hydrogen?

Q. 2. Explain Steam methane reforming process of hydrogen production.

Q. 3. Write note on direct electrolysis of water.

Q. 4. Explain in detail the biological method of hydrogen production.

Q. 5. Which are the various methods of hydrogen storage?

Q. 6. How we can utilize hydrogen for various purposes?

Q. 7. What is Fuel cell? Give the classification of fuel cells.

Q. 8. Write short note on Solid oxide fuel cell.

Q. 9. What are the advantages of the fuel cell?

Q. 10. Write potential applications of the fuel cell.

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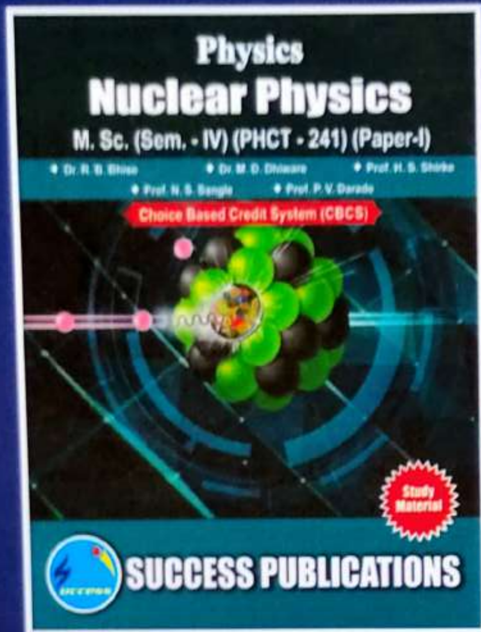

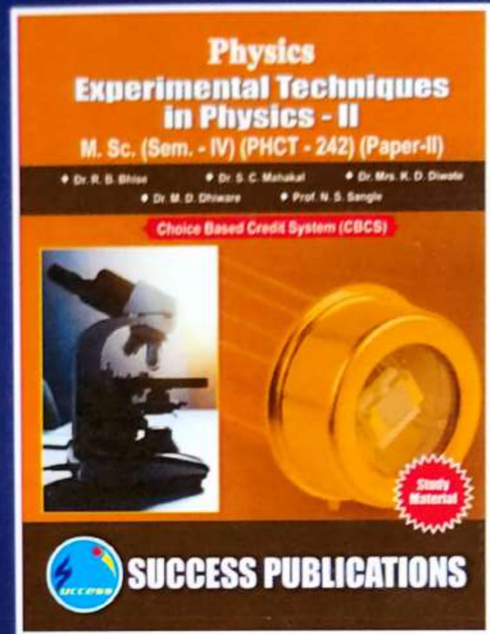

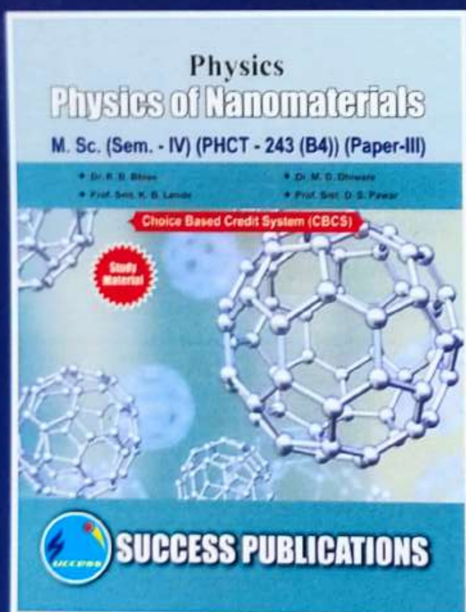

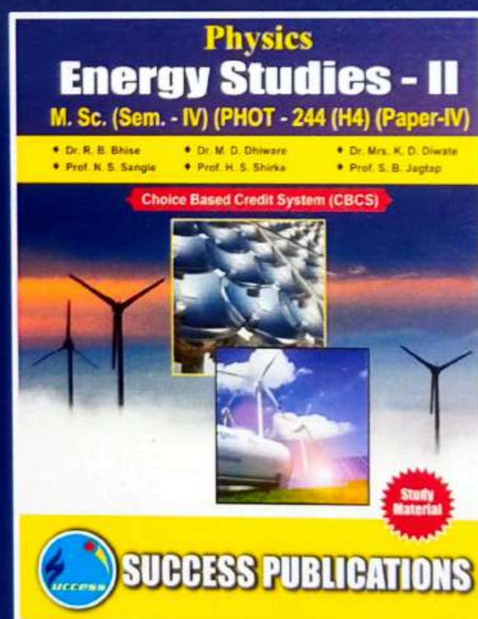

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