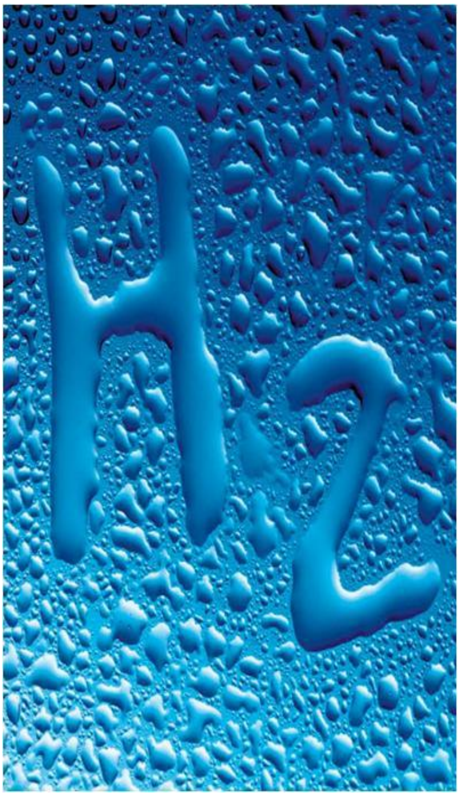
CHAPTER 1



Chapter 1

General introduction

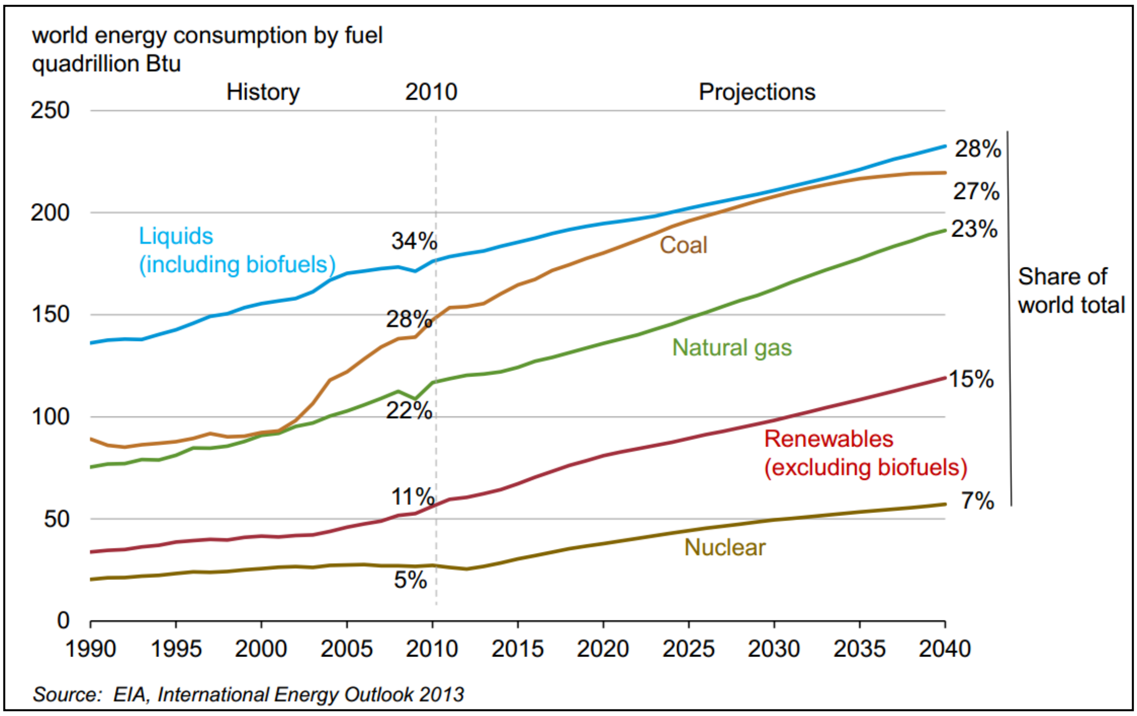
Contents

In this section of chapter, the worldwide energy demand and environmental issues due to current processes for energy conversion are discussed. A description is also given on hydrogen as a future energy carrier. Hydrogen production techniques which hold promise are also briefly discussed.

1.1 General

Energy is essential for human survival and socio-economic development. The worldwide energy consumption has been increasing gradually in recent years, and this inclination is expected to continue in the future. In the year 2016, the worldwide consumption of energy per year was equivalent to 13,275 Million tonnes of oil [1,2]. At present, our energy dependency is more than 75% on fossil fuels; human being is largely depended on fossil fuels to fulfil its energy needs. Moreover, intensified use of fossil fuels has also increased due to increased energy consumption. Fossil fuels are carbon based fuels such as coal, oil and natural gas [3]. Unfortunately, as these are non-renewable resources, the reserves are limited and may be worn out within a few coming decades.

Even in present time, energy shortage is becoming worldwide problem. The International Energy Agency (IEA) forecasts that world primary energy demand between now and 2030 will increase by 1.5% per year from just over 12,000 million tonnes of oil equivalent (Mtoe) to 16,800 Mtoe- an overall increase of 40% [Fig. 1.1]. Developing Asian countries are the main drivers of this growth, followed by Middle East. Moreover, the consumption per capita in India has also increased to 1,010 kilowatt-hour (kWh) in 2014-15, compared with ~950 kWh in 2013-14 and ~915 kWh in 2012-13 [Fig 1.2] [4]. Besides this high energy consumption, the demand for other energy sources (oil etc.) still depend mainly on foreign imports, and that is also continuously increasing over the years.



Source: EIA, International Energy Outlook 2013

Figure 1.1: World energy consumption [5].

Moreover, combustion of these carbon-based fossil fuels produces gaseous waste products. These gaseous products include sulphur dioxide, nitrogen oxides, hydrogen chloride, unburnt hydrocarbons and carbon monoxide which are air pollutants and contribute to the airborne particulate matter. Carbon dioxide (CO_2), which is the combusted product, is a greenhouse gas (GHG) responsible for global warming [6]. It increases the average temperature of earth affecting the equilibrium in all the ecosystems [7,8].

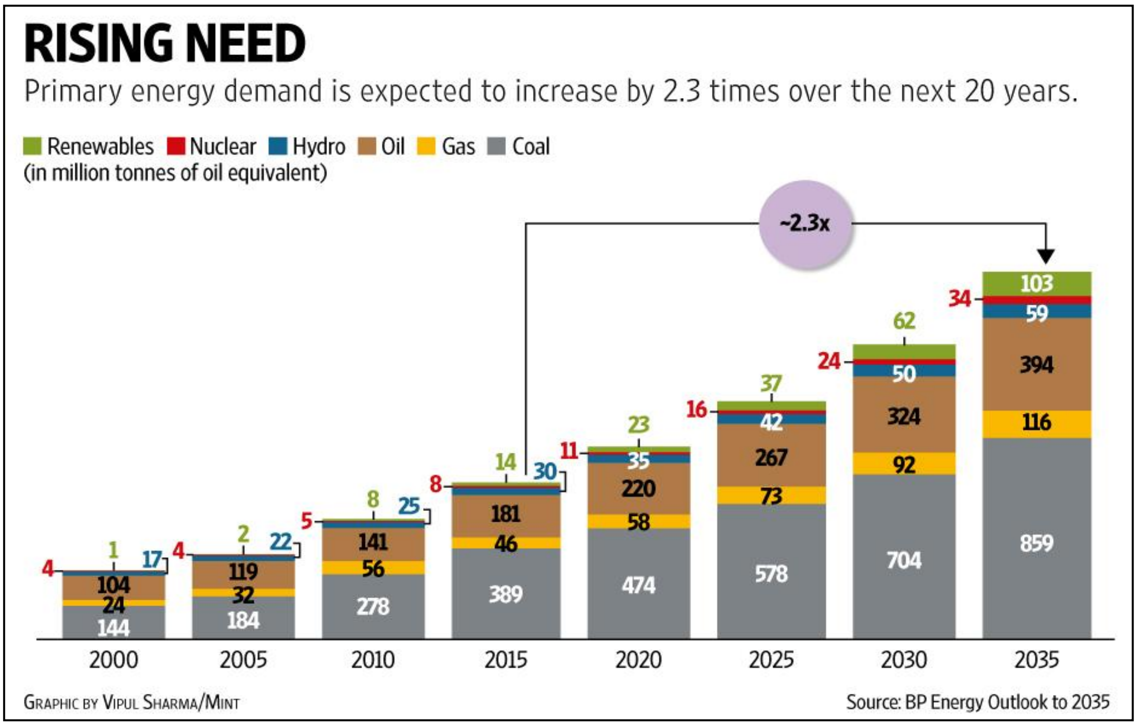


Figure 1.2: Energy consumption in India.

Table 1.1: Environmental impacts of fuels.

Pollutants	**Coal**	**Oil**	**Natural gas**	**Nuclear**
Global warming (CO_2)	√	√	√	
Acid pollutants	√	√	√	
Particulate matter	√	√		
Heavy metals	√	√		
Catastrophe & accidents	√	√	√	√
Waste disposal	√	√		√
Visual impacts	√	√	√	√

The environmental impact resulting from the use of these conventional energy sources has received attention all over the world in recent years. Table 1.1 provides the environmental impacts of these sources. It should be noted that about 75% of the world energy supply is fulfilled by consumption of fossil fuels.

Thus, there is an immense necessity to develop clean and alternative energy resources in order to decrease GHG emissions and air pollutants. Owing to above reasons, the worldwide attention is on the use of non-fossil fuel based energy resources especially which are renewable. In fact, renewable energy is already underway in transition globally. On one side, the price of oil and gas is fluctuating and on another side, more efficient systems to use renewable energy are being continuously developed. In the total energy requirement, as Fig. 1.1 and 1.2 illustrate, renewable energy collectively provides only about 7 percent of the world's energy needs, but it will have a higher share in the years to come. In future it will be deployed globally to replace fossil-dominated energy supply. It is no longer "alternate energy", but will increasingly become a key part of the solution to the nation's energy needs. Renewable energy offers the opportunity to lessen fossil fuel consumption. Energy derived from solar, wind, hydroelectric, geothermal, and biomass sources are considered renewable. Because most forms of renewable energy are derived either directly or indirectly from the sun, therefore unlike fossil fuels, there is an abundant supply of renewable energy available to us. The use of renewable energy also provides environmental, economic and political benefits.

The task to shift from fossil fuel based energy to renewable energy is overwhelming but can be achievable, because India has potential for generation of power from renewable energy source. As India has a large supply of renewable energy resources, it took a decision to organize a program for proper utilization of renewable energy resources. Solar energy is certainly the most abundant source of energy. The amount of solar irradiation receiving by earth surface is $3x10^{24}$ J/year, which is 10^4 times higher than annual world consumption [9]. Solar energy is a decentralized and inexhaustible natural resource. Energy provided by solar energy to the earth in one hour is equivalent to the energy consumed by humans in an entire year [10]. However, if solar energy is to be a major primary energy source then, because of daily and seasonal variability, it must be converted and stored to be used on demand. The important steps for development of renewable energy sources taken government are recapitulated below:

India took the prevalent renewable energy capacity expansion programme. The government intended to raise the share of clean energy through renewables. Currently, the Ministry of New and Renewable Energy (MNRE) has set up a Solar Energy Centre near Delhi with the state-of-art facilities for testing of solar thermal and solar photovoltaic materials, devices and systems. This will soon become an apex Centre of Excellence. Current vision of MNRE is "to upscale and mainstream the use of new and renewable energy sources in furtherance of the national aim of energy security and energy independence, with attendant positive impact on local, national and global environment". It is planned that that India will achieve 40% cumulative Electric power capacity from non-fossil fuel based energy resources by 2030 [11].

Solar energy is one of most primary source of renewable energy [12,13]. It is a clean and plentiful energy source on earth. The territorial area of India is about 3,287,262 km^2 with 7,516.6 Km coastline frontier. The annual average solar radiation received by India is 200 MW/km^2 [14]. Various technologies are available to utilize solar energy. But those have some flaws like inconsistency, inefficiency, and high initial capital outlay [15,16]. When the sun is not shining, energy cannot be generated. Also, amount of sunlight that is received on the earth depends on location, time of day, and weather conditions. Therefore, as a renewable source of energy, solar energy can be harvested in the form of heat, electricity, and hydrogen. Solar energy stored in the form of Hydrogen (H_2) may become a possible solution to a long-term supply from the renewable energy sources [17]. Moreover, in the development of new energy sources, hydrogen is one of the most attractive fuels for the 21st century. In addition, the combustion of hydrogen produces water without GHG emission and air pollutants [18]. Therefore, Sustainable hydrogen production is a key target for the development of alternative future energy systems that will provide a clean and affordable energy supply.

1.2 Hydrogen as an energy carrier

Hydrogen is a promising non-fossil fuel energy carrier. It has many positive attributes [Table 1.2];

Table 1.2: Comparisons of combustion properties of Hydrogen to methane and propane [20, 21]

Combustion property	**Hydrogen**	**Methane**	**Propane**
Heating value (MJ/Kg) H_u	140	55.5	50.35
Flame temperature (K)	2400	2228	1750
Flame speed (cm/s)	281	40.5	47
Flammability limits (vol %)	4 – 75.6	5 – 15	2.5 –9.3
Ignition temperature in air	530 °C	645 °C	510 °C
Quenching distance (mm)	<< 1	>1	<1

Hydrogen (H_2) has the highest energy content per unit mass [Table 1.3]. It has heating value of 140 $MJ.kg^{-1}$ that is three times larger than liquid hydrocarbon based fuels [19].

Table 1.3: Combustion values of hydrogen and fossil fuels [24].

Energy source	**Combustion value (MJ/Kg)**
Hydrogen	140
Biogas (CH_4)	50
Natural gas	49
Liquefied petroleum gas	46
Gasoline	45
Coal	29

Furthermore, hydrogen can be added with other fuels in order to form energy-enriched mixtures. Due to its wide flammability range, it allows easy engine power control. It could be also used as an alternative fuel for engines [22]. Hydrogen has the lowest flashpoint (–230 ^{o}C) compared to another available common fuels. Flashpoint is the temperature at which a fuel generates adequate vapour to form a flame at its surface [23]. Therefore, it is expected that hydrogen based engines require less sophisticated equipment to start and ignite compared to others. In addition, hydrogen possesses a higher octane number of 130 [21]. Hydrogen has a very high (laminar) flame speed. Its value is higher than that for gaseous hydrocarbons [21]. Moreover, another feature is low ignition delay time. These properties allow hydrogen flames to be stabilized in areas with high flow velocity and very fuel rich conditions which are not accessible for flames fuelled by gaseous hydrocarbons.

While hydrogen energy has a lot of admirable properties, it has a few drawbacks also. It has a high diffusivity. While its gives it an edge over energy sources in terms of accomplishing numerous tasks, it equally renders it risky to use and work around. One key disadvantage to hydrogen is the difficulty of storing it. Hydrogen needs to be kept under strong compression (physical storage) [25]. Recently, chemical storage is also becoming an option, where hydrogen is stored as solid hydrides but these are still under research [26–29].

Further hydrogen is abundant on the earth but not available in free form on the earth. It is found in the form of water (combines with other elements oxygen) or hydrocarbons and coal (combines with carbon). It is not a primary source, and hence, it needs to be produced.

1.3 Hydrogen production techniques

At present, commercial processes are based on:

- Processing of carbonaceous materials mainly natural gas or naphtha.
- Electrolysis of water

1.3.1 By processing carbonaceous matter

Essentially any carbonaceous matter can be processed by the following processes for hydrogen production

(a) Steam reforming

(b) Partial oxidation

(c) Oxidative steam reforming

(a) Steam reforming

Steam Reforming (SR) of naphtha or natural gas is still the main industrial process for the production of H_2 specially SR of natural gas [30,31]. Main component of Natural Gas is methane (CH_4), which hydrocarbon has the highest H/C ratio. SR catalysts are typically nickel based catalysts [32,33]. A block diagram of the SR process is shown in Fig. 1.3. Three steps are involved in SR of natural gas: The first step is to react the feedstock consisting of light hydrocarbons, usually methane (CH_4), with steam at elevated temperatures (700 °C to 900 °C) to produce syngas – a mixture of hydrogen (H_2) and carbon monoxide (CO). The second step, a water-gas shift reaction, the component of the syngas carbon monoxide reacts with steam to produce additional H_2 and carbon dioxide (CO_2). This shift reaction is used to increase the H_2 content. Finally, a mixture of CO_2 and H_2 is sent to a gas purifier where the hydrogen is separated from CO_2 via one of many methods (pressure swing absorption, wet scrubbing or membrane separation). Initially, in this process, sulphur is removed from the hydrocarbon feed stocks because sulphur is a poison for SR catalysts and process equipment.

$$\mathrm{CH_4 + H_2O \leftrightarrows CO + 3H_2 \quad \Delta H = +206\ kJ/mol} \tag{1.1}$$

On the other hand, for higher hydrocarbons:

$$\mathrm{C_nH_m + nH_2O \leftrightarrows nCO + \frac{(m+n)}{2} H_2} \tag{1.2}$$

Simultaneously in high- and low-temperature shift reactors, the so-called water gas shift reaction produces further H_2 according to the exothermic equation:

$$\mathrm{CO + H_2O \rightleftarrows CO_2 + H_2} \quad \Delta H = -41\ \mathrm{kJ/mol} \tag{1.3}$$

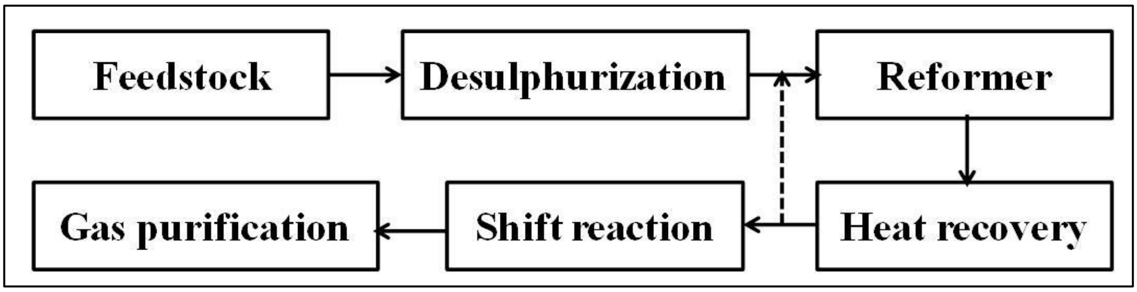


Figure 1.3: Flow diagram of steam reforming of hydrocarbon.

Steam reforming is normally carried out at the temperature range of 700-900^{o}C and pressure is about 0.1–0.3 MPa. Major drawback is generation of greenhouse gases also [34].

(b) Partial oxidation

Partial oxidation reaction (POX) is an alternative route to produce H_2 gas starting from hydrocarbon feedstock [35]. In partial oxidation, natural gas containing the methane and other hydrocarbons react with oxygen which is present in a limited amount. Products from this reaction are H_2 and CO (and N_2, if air is used a source of O_2 instead of pure oxygen) in place of CO_2 and H_2O. CO_2 is produced relatively in a small amount. Subsequently, CO reacts with H_2O to form CO_2 and more H_2 in a water-gas shift reaction. Partial oxidation is an exothermic process. Typically this process is faster and a smaller reactor vessel is required rather than steam reforming. Operating conditions provided are the temperature range of 700–1000 ^{o}C and atmospheric pressure. The catalysts used in POX are typicaaly noble metals such as Pt, Ru, Pd, or Rh and transition metals such as Ni, Co dispersed onto appropriate support [36]. The stoichiometric equation for hydrocarbon (methane) conversion is following:

$$\mathrm{CH_4} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO} + 2\mathrm{H_2} \quad \Delta\mathrm{H} = -35.6\ \mathrm{kJ/mol} \tag{1.4}$$

or, for higher hydrocarbons:

$$C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2 \tag{1.5}$$

Oxygen present in air is utilized for this reaction as oxidant. This process involves the combustion of hydrocarbon feedstock in a flame where requirement of stoichiometric oxygen for complete combustion is less. Carbon dioxide (CO_2) and water (H_2O) are produced according to Eq^{n}s. 1.6-1.8:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -801.6\ kJ/mol \tag{1.6}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H = -282.7\ kJ/mol \tag{1.7}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H = -241.6\ kJ/mol \tag{1.8}$$

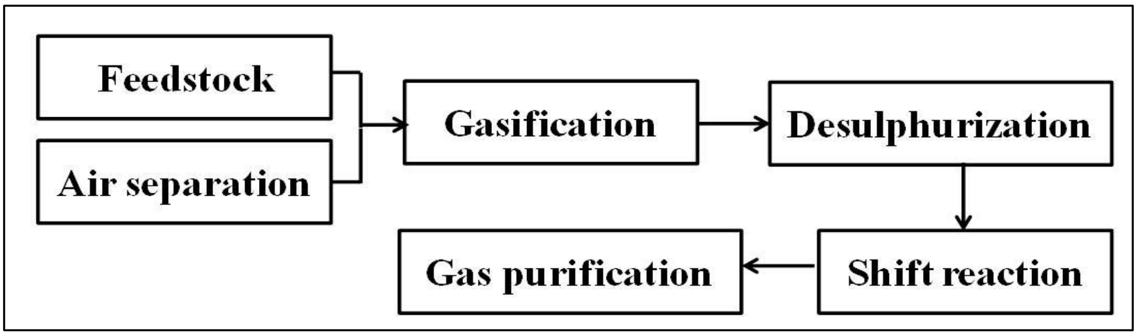


Figure 1.4: Flow diagram of partial oxidation process.

A schematic representation of the POX process is shown in Fig. 1.4. The external energy required to drive the process is obtained through the combustion of the feedstock itself. As a result, pollutants such as NOx, SOx and CO_2 can be generated in the process; to minimize the production of NOx, the air input to the process must be separated so that pure oxygen is supplied to the reformer. This results in the need for an air separation plant which increases the capital cost of the POX plant and results in a more expensive hydrogen product. The unreacted hydrocarbon produces carbon monoxide and hydrogen [37]. Major drawback is requirement of pure oxygen and generation of more CO_2 than steam reforming.

(c) Oxidative steam reforming

Oxidative steam reforming (OSR) method uses the exothermic partial oxidation to provide the heat for endothermic steam reforming. Basically, steam with oxygen or air, are injected into the reformer, causing the reforming and oxidation reactions to occur simultaneously, as shown in Eq^n. 1.9 [38, 39]:

$$C_nH_m + \frac{n}{2}H_2O + \frac{n}{4}O_2 \rightarrow nCO + (\frac{m}{2} + \frac{n}{2})\ H_2 \quad (1.9)$$

In Fig. 1.5, a simplified flow diagram of the OSR is available presenting the process explained by Eqn. 1.9. Optimal operating conditions for OSR are 700–800 ^oC temperature, 0.7–1.0 O/C (oxygen to carbon) ratio and 1.5–2.0 S/C (steam to carbon) ratio. Transition metals are known to be active catalyst for OSR. Most metals that are active for SR and POX individually are also active for OSR [40]. Cost of this technology is high due to Oxygen separation. Moreover, steam requires a water storage and supply system, which adds weight, complexity, and cost to the process.

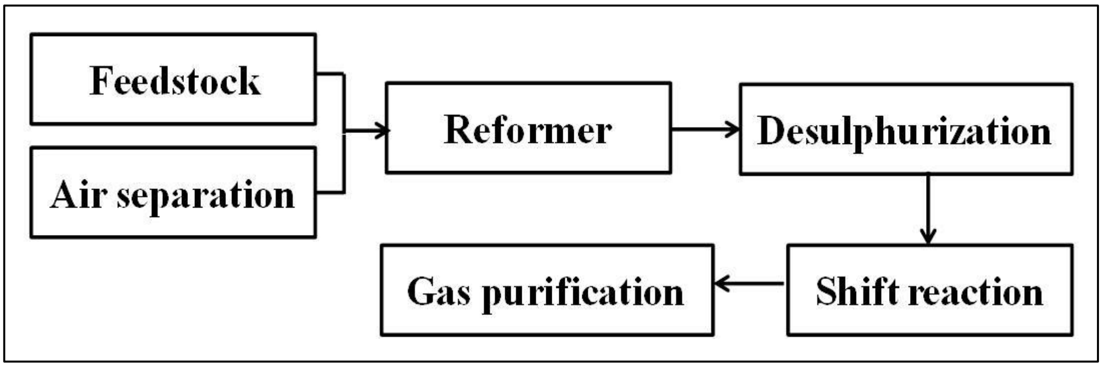


Figure 1.5: Flow diagram of oxidative steam reforming.

(d) Other Methods

Another important method for hydrogen production based on thermal process is the coal gasification process. It is mainly used to generate electricity on industrial scale essentially. It is also the oldest method for H_2 production. By this process, any kind of organic material, such as coal, biomass derived mixtures or other petroleum can be converted [41,42]. In general, coal is selected feedstock (as reference carbonaceous fuel), the following (not balanced) overall chemical equation for gasification process can be written as:

$$CH + O_2 + H_2O \leftrightarrows CO + CO_2 + H_2 \qquad (1.10)$$

At temperatures ranging from 1000 to 1500 ^{o}C, producing carbon-oxides and H_2 gaseous mixtures and simultaneously also char (pyrolysis) are produced after volatizing of feedstock. After introduction of oxygen or air in limited quantity into the reactor mixed with crushed/pulverized coal feed, it reacts with char to form CO_2 and CO. The basic reactions:

$$C + \frac{1}{2}O_2 \rightarrow CO\ \Delta H = -110.4\ \mathrm{kJ/mol} \qquad (1.11)$$

$$C + O_2 \rightarrow CO_2\ \Delta H = -393.1\ \mathrm{kJ/mol} \qquad (1.12)$$

The main advantage of this technology is that CO_2 can be easily separated from the syngas and then captured, instead of being released into the atmosphere [27]. If oxygen is used in a coal gasifier instead of air, carbon dioxide is emitted as a concentrated gas stream in syngas at high pressure.

Biomass gasification is also a promising method in which biomass is converted into H_2 by heat, steam, and oxygen without combustion [43]. Generally, Biomass is carbon neutral sources. These are agriculture crop residues such as wheat straw or corn stover, special crops like willow trees or switch-grass (these are grown for especially energy use), forest residues, organic municipal solid waste, and animal wastes.

1.3.2 Electrolysis of water

A well-known electrochemical method to produce H_2 using electricity is the water electrolysis [44–46]. It permits the splitting of water molecule into H_2 and O_2. In this process, a chemical reaction i.e. water electrolysis takes place by external electric energy in an electrochemical cell. The reaction, however, is very endothermic thus the required energy input is provided by electricity.

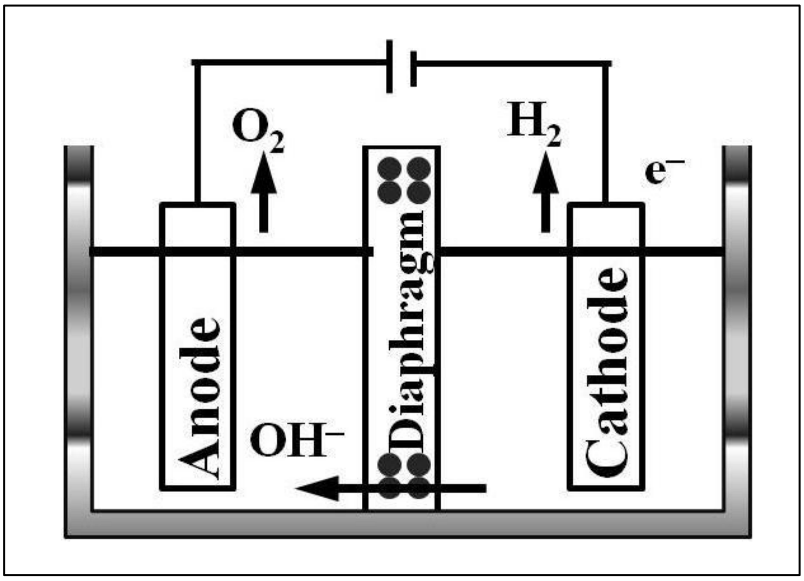


Figure 1.6: Schematic representation of electrolysis of water.

Water decomposition by electrolysis consists of two half reactions that take place at two electrodes separated by an ion-conducting electrolyte as shown in the Fig. 1.6. H_2 and O_2 are produced at the cathode and the anode, respectively. An ion-conducting separator (diaphragm) is used to separate the two chambers to keep the produced gases isolated from each other. The electrodes are used to apply a voltage to the water causing the water separation as seen in the following reaction:

$$H_2O \rightarrow H_2 + O_2 \quad (1.13)$$

For the simplest case of electrolysis at 25 °C and 1 atm, the potentials of the electrode and cathode can be written as:

$$E_C = -0.828 - 0.059 \log a_{OH^-} \quad (1.14)$$

$$E_a = 0.401 - 0.059 \log a_{OH^-} \quad (1.15)$$

Where, '*a*' is the activity. The lowest voltage needed to drive the water splitting reaction is E_a–E_c = 1.229 V (this is called the reversible or equilibrium voltage).

Many types of electrolyzers exist today. In general, potassium hydroxide (KOH) is used as electrolyte in solution (alkaline solution). Operating temperature is at about 80 °C. Today, this technology gives a very low contribution to the worldwide hydrogen production, because of the high cost of electricity and the high but not complete conversion efficiency [47].

In electrolyzers, because of the low conductivity of water, some chemical solutions must be added to increase the solution conductivity. Strong acid and strong alkali are applied as an electrolyte. Due to the severe corrosion of acid, instead of strong acid, the alkaline solutions are the primary electrolytes for water electrolysis. As an alternative to alkaline electrolysis, PEM (or polymer electrolyte membrane) electrolysis technology uses solid polymeric ion exchange materials in the electrolyzer [48,49]. The major R&D challenge for the future is to design and manufacture electrolyser equipment at lower costs with higher energy efficiency. Another problem of electrolysers is the limited lifetime of the electrolysis cells.

Similar to water electrolysis, High temperature steam electrolysis (HTSE) is an electrolytic process as well, but instead of water steam is fed to the electrolyzers at the temperature of 700–1000 ºC [50]; electrolyzers of HTSE are also different from water electrolysis. The reactions at the anode and the cathode are shown as follows [51]:

Cathod reaction: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$ (1.16)

Anode reaction: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$ (1.17)

Net reaction: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (1.18)

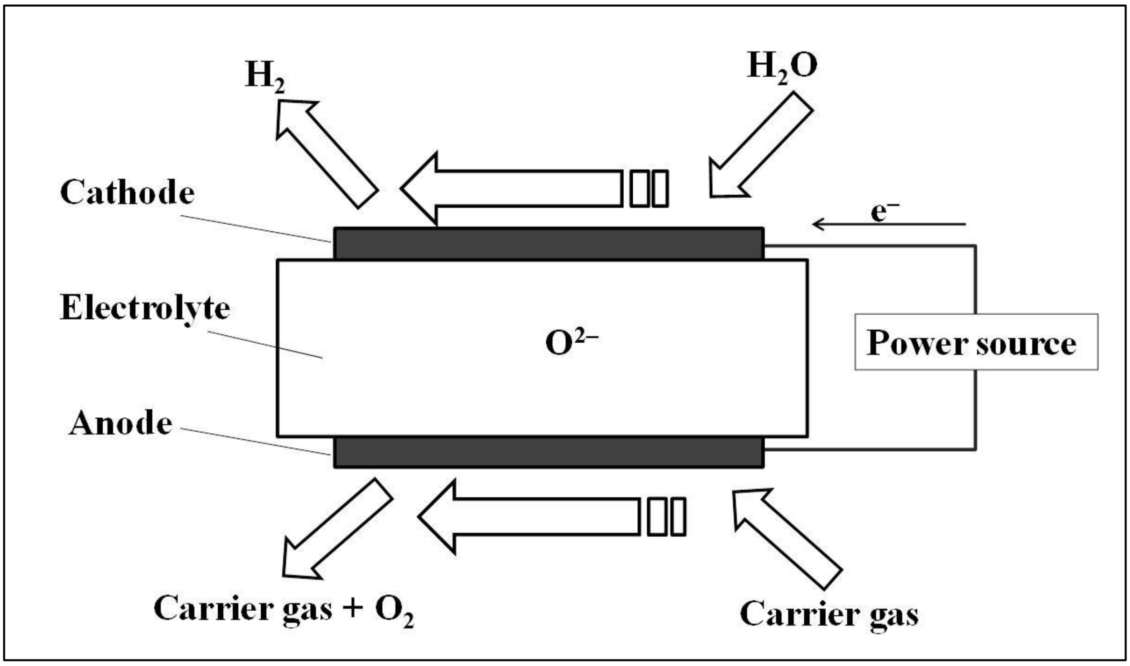


Figure 1.7: Schematic representation of high temperature steam electrolysis.

A schematic representation of HTSE is illustrated in Fig. 1.7. In this process, steam is supplied to the electrolyzer to dissociate it into hydrogen gas and oxygen ions. Hydrogen gas is accumulated and generated at the cathode while oxygen ions pass through the dense electrolyte and receive electrons to generate oxygen gas at the anode.

Compared with conventional water electrolysis, heat is introduced and less electricity is consumed in HTSE. The efficiency of HTSE from heat to hydrogen is projected to be up to 55%; with regard to energy loss from electricity generation, theoretically the efficiency from heat to hydrogen in HTSE is higher than water electrolysis due to less power consumption [51].

1.4 Solar hydrogen systems

Sustainable hydrogen production is a key target for the development of alternative future energy systems that will provide a clean and affordable energy supply. Moreover, it is carbon-free and also renewable hydrogen production.

Hydrogen can be produced using a renewable source, i.e. solar energy and it dissociation from water, which is abundant on earth. These systems are solar hydrogen systems.

Four different processes are being investigated by scientists around the world to harvest solar energy for dissociation of water, as given below:

- Photovoltaic cell plus electrolyzer,
- The photoelectrochemical (PEC) system that uses photoactive cells/photoelectrodes,
- The photobiological (PB) water splitting, and
- Photocatalytic process.

1.4.1 Photovoltaic cell plus electrolyzer

It is two step processes. At first, electricity is produced by PV panels. The electricity is utilized for electrolysis of water. Direct current is passed through water to generate hydrogen to conduct electrolysis [52,53]:

$$2H_2O + \text{Electrical energy (from Solar PV)} \rightarrow 2H_2 + O_2 \quad (1.19)$$

The PV cell is composed of semiconductor material that makes it uniquely capable of converting light into electricity. When light shines on a photovoltaic (PV) cell, light is absorbed by a semiconductor; photons of light can transfer their energy to electrons, allowing the electrons to flow through the material as electrical current. This current flows out of the semiconductor to metal contacts and then makes its way to the electrolyser to dissociate water [Fig. 1.8]. Gibson et al. [54], Bhattacharyya et al. [55], and Yilanci et al. [56] analyzed the efficiency, effectiveness and cost of this method for large and low scale hydrogen generation applications. This method is presently costly (>$5/kg H_2) and generates hydrogen at very low efficiency (<5%).

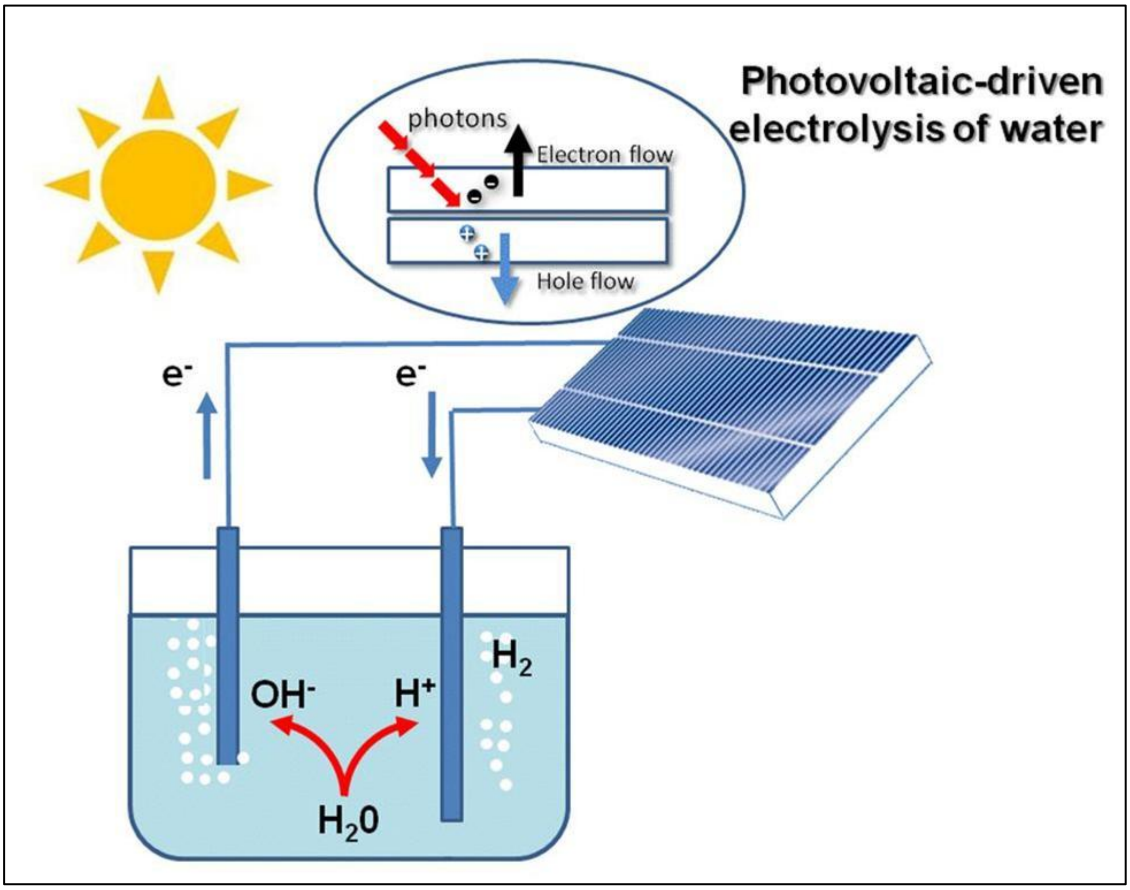


Figure 1.8: Schematic representation of a photovoltaic cell plus electrolyzer system.

1.4.2 Photo-electrochemical process

A PEC process consists of electrolyzer having a semiconductor electrode of desired bandgap [57–60]. When light falls on this semiconductor electrode, it generates electron–hole pairs. These electrons are forced to move by an external bias to another electrode, where it produces H_2 by dissociation of water. Holes are utilized by the sacrificial agents present in the electrolyte [Fig. 1.9]. For example if sulphide and sulphite ions are presented in electrolyte [61]:

$$\mathrm{CdS} \overset{h\upsilon}{\rightarrow} \mathrm{CdS}^* + h^+ + e^- \quad (1.20)$$

$$2H_2O + 2e^- \rightarrow 2H_2 + 2OH^- \quad (1.21)$$

$$2S^{2-} + SO_3^{2-} + 2h^+ \rightarrow S_2O_3^{2-} \quad (1.22)$$

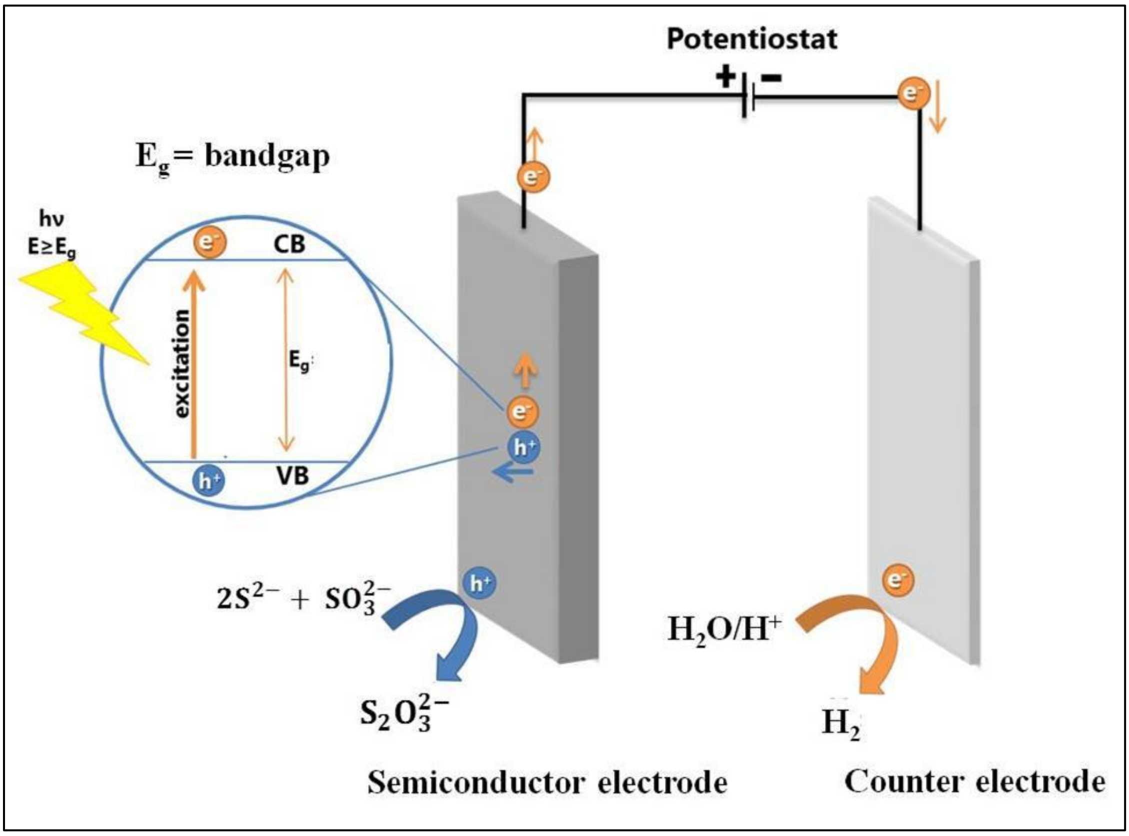


Figure 1.9: Schematic representation of a photoelectrochemical system.

1.4.3 Photo-biochemical (bio-photolysis) process

This process is similar to a photo-electrochemical cell. In presence of solar radiation, blue-green algae dissociate water into hydrogen [62]. The feed for bio-hydrogen are water for photolysis where hydrogen is produced by some bacteria or algae directly through their hydrogenase enzyme.

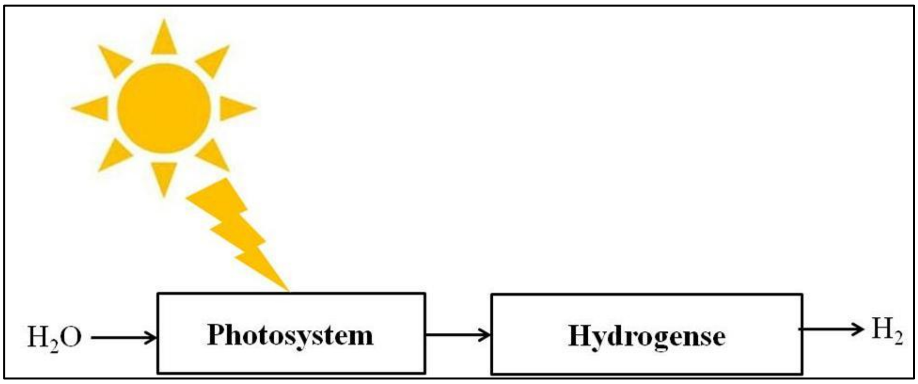


Figure 1.10: Flow diagram of the bio-photolysis process.

Bio-photolysis is a biological process in which principle is similar to plants and algal photosynthesis, but adapts them for the generation of H_2. In green plants only CO_2 reduction takes place. On the contrary, algae contain hydrogen-producing enzymes and can produce hydrogen [63,64]. Green algae are able to split water molecules into hydrogen ions. In direct bio-photolysis, green algae split water molecules to hydrogen ion and oxygen via photosynthesis, as shown in Fig. 1.10. The generated hydrogen ions are then converted into hydrogen gas by hydrogenase enzyme. This enzyme is very sensitive to oxygen, and thus, it is necessary to maintain the oxygen content at a low level under 0.1%. The capital cost is quite high; it implies higher production cost [65].

1.4.4 Photocatalytic process

Photocatalytic water splitting is a general term used for the dissociation of water into hydrogen (H_2) under solar radiation. Photocatalytic water splitting has the simplicity. It just uses catalyst powder in solution and sunlight to produce H_2 from water. There is no side production of greenhouse gases or any adverse effects on the atmosphere. Theoretically, only solar energy (photons), water, and photocatalyst (a semiconductor) are needed.

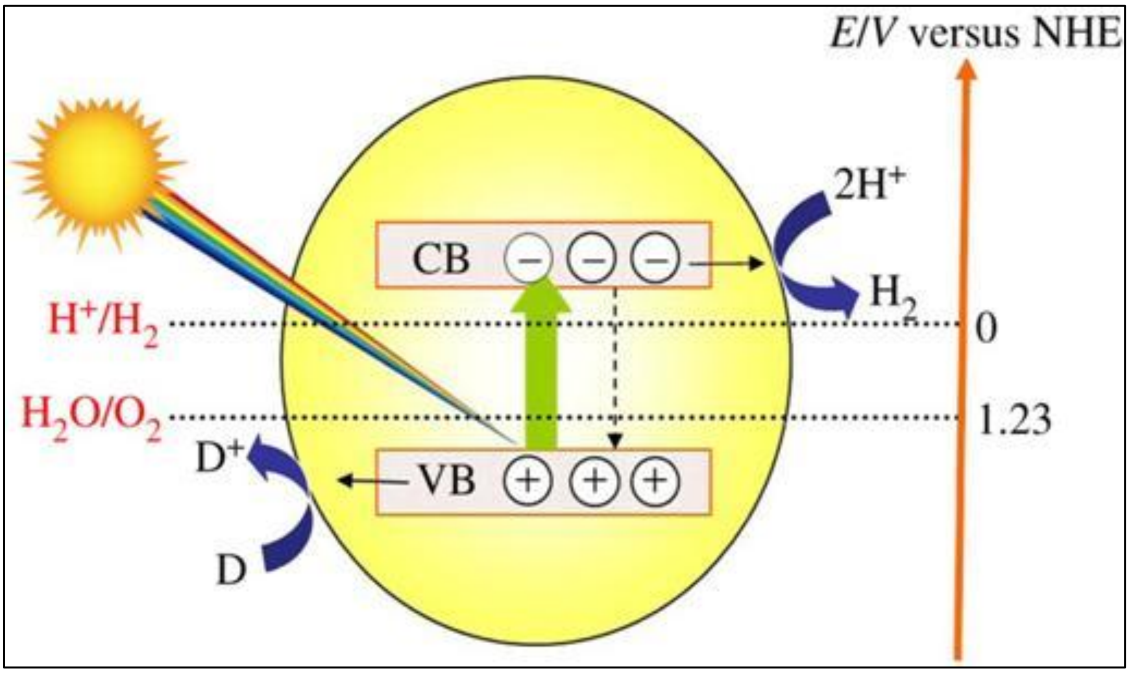


Figure 1.11: Schematic representation of a photocatalysis process for H_2 production.

Various studies are reported [66–68] in the literatures which focus on colloidal systems; photocatalyst particles are suspended in an electrolyte within a glass batch reactor. No external bias is applied/ required, so the particles act naturally as a functioning anode and cathode [Fig. 1.11], where oxidation and reduction reaction take place.

Various reviews articles are published for hydrogen production techniques. Nikolaidis et al. [69] gave a comparative overview of hydrogen production processes. Kothari et al. [70] compared the environmental and economic aspects of various hydrogen production methods. Dincer et al. [71] presented comparative environmental, technical, financial, and social assessments of 19 possible hydrogen production methods. Hosseini et al. [72] an overview of the state-of-the-art hydrogen production technologies using renewable and sustainable energy resources. Acar et al. [66] also discussed advantages and disadvantages of various hydrogen production methods, with a particular emphasis on photocatalytic hydrogen production. Momirlan et al. [73] also reported the progress of the recent directions of world hydrogen production, with emphasis on photocatalytical hydrogen processes. Acar et al. [74] presented comparative impact assessment of possible hydrogen production methods including environmental & social impact, cost, energy and exergy efficiencies. Although, renewable methods specially photocatalytic process are not competitive in terms of cost-effectiveness, but renewable feedstocks and direct conversion of solar energy in hydrogen i.e. present obvious advantages and have gained significant attention over the last years.

Mostly commercial hydrogen is produced by steam forming of natural gas and its sells at ~Rs. 45 per kg. At the current state of development of processes for solar hydrogen, the price would be approximately 10 times higher.

Overall, Hydrogen is an excellent energy carrier with many unique properties. It is an efficient and cleanest fuel. Hydrogen can be produced by dissociation of water and on combustion it reforms water. Thus, it is completely renewable and does not produce any pollutant. It potentially offers the cleanest and sustainable way to produce hydrogen. However, the exploration for suitable semiconductor to be employed for the water dissociation into hydrogen is still an open challenge.