1 Introduction

In this section of the thesis, discuss about the current energy demand and different environmental issues in the world have been discussed. A description is focused on renewable energy and alternative energy resources which have the potential to overcome the energy carries. This section also discussed the techniques used for hydrogen production.

1.1 General

Energy is essential for all living organism to survive. The worldwide energy consumption has been increasing gradually and this inclination is expected to continue in the future. Main cause for the inclination of this energy demand is a due to increase in population with a high rate. At present global energy demand is largely fulfilled by carbon based fossil fuels. However, these energy sources are depleted day by day. Presently, according to BP statistical review of world Energy[1],the growth rate of 2.2% per annum experienced from 1971 to 1995. In absolute terms, the annual global demand for energy increased from 8341 Mt in 1995 to 13,749 Mt in 2020.Figure 1 shows the global reserve of conventional energy resources. These values however change with time based on new discovery and change in annual production. Moreover, combustion of these carbon-based fossil fuels produces gaseous waste products. These gaseous products include sulphur dioxide, nitrogen oxides, hydrogen chloride, un-burnt 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 [2]**.** It increases the average temperature of the earth affecting the equilibrium in all the ecosystems [3, 4]. 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.

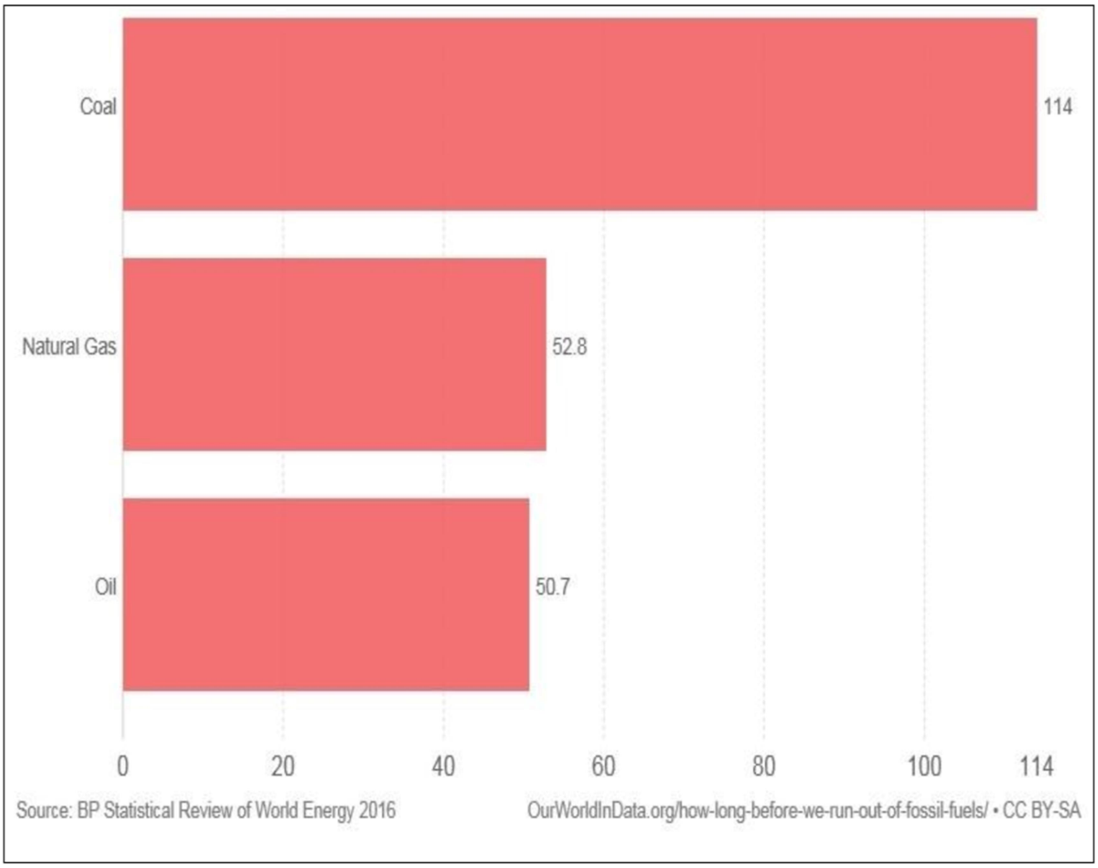

Fig 1.1: Years of global coal, oil and natural gas left, reported as the reserves-to-product (R/P) ratio which measures the number of years of production left based on known reserves and annual production levels in 2015.

Thus, there is an immense necessity to develop clean and alternative energy resources in order to decrease GHG emissions and air pollutants. Owing to the above reasons, 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 continuously developed. In the total energy requirement, as Fig. 1.2 illustrate, renewable energy collectively provides only about 7% 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.

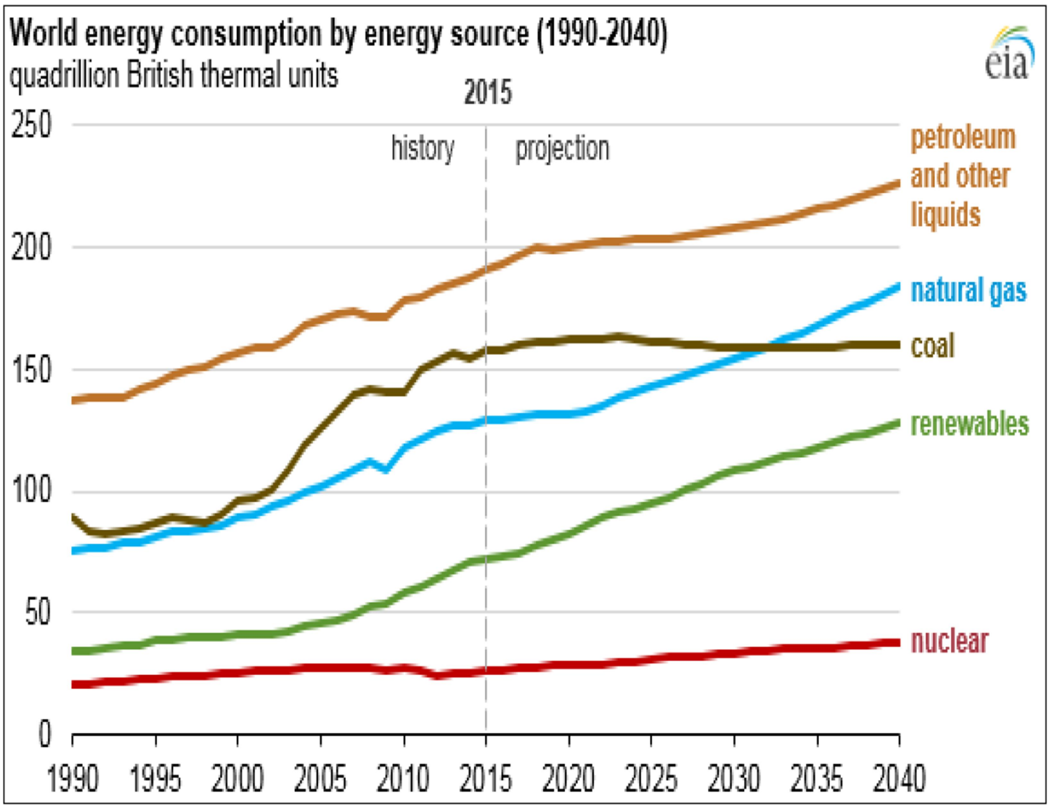

Fig 1.2 World energy consumption

The task to shift from fossil fuel based energy to renewable energy is overwhelming but can be achievable.

Table 1.1 Environmental effects of fuels

Pollutants	Coal	Oil	Natural Gas
Global warming	√	√	√
Acid Pollutants	√	√	√
Particulate Matter	√	√	
Heavy Metals	√	√	
Water Disposal	√	√	
Visual Impact	√	√	√

Solar energy is the most primary source of renewable energy [5, 6]. 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[7]. Various technologies are available to utilize solar energy. However, these have some limitations like inconsistency, inefficiency, and high initial cost [8, 9]. When the sun is not shining energy cannot be generated. Also, the amount of sunlight that is received by the earth depends on location, time of day, and weather condition. Therefore, as a renewable source of energy, solar energy can be harvested in the form of thermal Energy, electricity, and chemical Energy (hydrogen). Solar energy stored in the form of hydrogen (H_2) may become a possible solution to a long- term supply from renewable energy sources [10]. Moreover, in the development of a new energy source, hydrogen is one of the most attractive fuels for 21st century. In addition, the combustion of hydrogen produces water without CHG emission and air pollutant [11]. 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

The most common element in the universe is hydrogen. A molecule of hydrogen contains the highest energy per unit weight of any known fuel. Hydrogen is not the primary source of energy because it is always available in a combined state. Hirscheret al.[12] reported that the energy per unit mass content of hydrogen is 143MJ/Kg, which is upto three times larger than liquid hydrocarbon-based fuels. On the other hand, it has a drawback that, it has a very low density in the gaseous state and liquefying is an energy consuming process. The comparison of the combustion properties of hydrogen with alkane is listed in Table 1.2.[13, 14].

Table 1.2 Combustion properties of hydrocarbon

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 Limit (vol%)	4 - 75.6	5 - 15	2.5 - 9.3
Ignition temperature in air (K)	803	918	783
Quenching distance (mm)	<< 1	> 1	> 1

In contrast, hydrogen has very long term viability. Hydrogen can also be added with other fuels in order to form energy enriched mixture. Other properties like flash point of hydrogen are lowest (−230˚C) among other available fuels. Therefore, it is expected that hydrogen based engines require less effort to ignite compared to other fuels. In addition, it has the highest octane number (130) and very high flame speed

[15]. These properties allow hydrogen flames to be stabilized in areas with high flow velocity and very fuel rich condition.

While hydrogen has a lot of admirable properties, it has a few drawbacks also. Such as, it has high diffusivity and high inflammability. Inflammability would add some extra and unnecessarily new risk into society. One most important disadvantage to hydrogen is the difficulty in its stores.

Table 1.3: Combustions values of hydrogen and fossil fuels [13]

Energy Source	Heat of combustion (MJ/Kg)
Hydrogen	140
Biogas (CH_4)	50
Natural gas	49
Liquefied petroleum gas	46
Gasoline	45
Coal	29

1.3 Hydrogen production techniques

Presently, there are two commercial processes

- Conventional method by carbonaceous matter as feedstock
- Dissociation of water

1.3.1 By Carbonaceous matter

Any or combination of three processes as given below as utilized

(a) Steam reforming

(b) Partial oxidation

(c) Oxidative steam reforming

(a) Steam reforming

It is the main industrial process for the production of hydrogen, carbon monoxide at temperature (700˚C to 900˚C) and high pressure[16]. Steam reforming (SR) is primarily suitable for light hydrocarbon, i.e., Natural gas. Natural gas mainly contains methane, which has a high H/C ratio. SR catalyst is typically nickel-based catalysts[17, 18].This is also called steam of natural gas reforming. A block diagram of the SR process is shown in Fig 1.3.

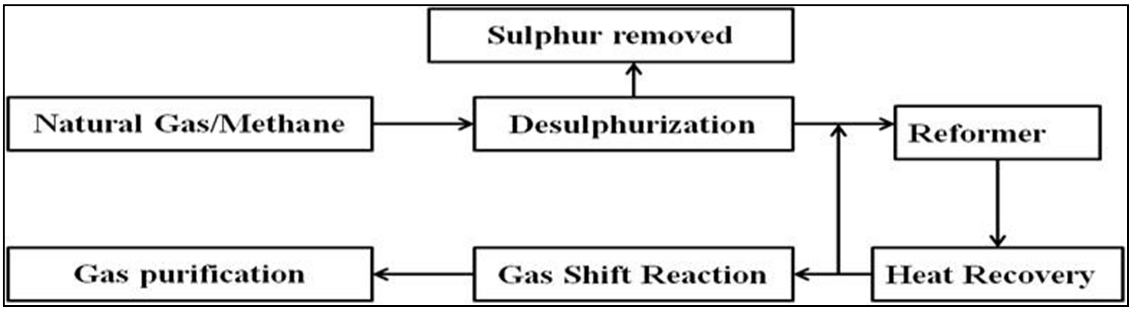

Fig 1.3 Flow diagram of steam reforming

There are three steps involved in the steam reforming process. In the first step, the light hydrocarbon usually methane takes steam at high temperature to produce syn gas (H_2+ CO). These cond steps, water gas shift reaction takes place by which CO of syn gas is converted into carbon dioxide and additional hydrogen gas by using steam. This shift reaction is important for additional hydrogen content. In the final step, the mixture of CO_2 and $H_2$is separated in the purifier section.

The reaction involving in SR process is written below

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = +206\ \mathrm{kJ/mol} \qquad (1.1)$$

On the other hand for higher hydrocarbons

$$C_nH_m + mH_2O \leftrightarrow nCO + \frac{(m+n)}{2}H_2 \quad (1.2)$$

The water gas shift reaction at low and high temperature is taking place simultaneously for the production of hydrogen.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41\, kJ/mol \quad (1.3)$$

When steam reforming process is carried out at high temperature (850˚C) and high pressure (0.1 - 0.3 MPa) is called high-temperature steam reforming. Nickel supported on alumina is used as a catalyst for high-temperature steam reforming. When steam reforming is carried out at about 500˚C, then the process is called low-temperature steam reforming. Nickel, platinum etc. noble metals are used as catalyst for low-temperature steam reforming [19].The major drawback is the generation of greenhouse gases.

(b) Partial oxidation

It is energy efficient and it produces syn gas with H_2/CO ratio of about 2 which is suitable for gas liquid technology. Partial oxidation process (POX) is generally exothermic reaction in which natural gas or heavy hydrocarbon is reacted with oxygen at high temperature and atmospheric pressure, to produce hydrogen [20]. If air is mixed instead of pure oxygen, then the product is H_2, CO and N_2 otherwise only H_2 and CO. Further, CO reacts with H_2O to form CO_2 and more H_2 in a water-gas shift reaction. Generally, this process is faster and smaller reactor vessel is required rather than a steam reforming process. Pt, Ru, Pd, or Rh and transition metals such as Ni, Co are used as a catalyst for POX reaction [20]. The stoichiometric equation for methane conversion is written below:

$$CH_4 + O_2 \rightarrow CO + 2H_2 \ \Delta H = -35.6 \text{ kJ/mol} \quad (1.4)$$

or, for higher hydrocarbons:

$$C_mH_n + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2} \quad (1.5)$$

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 reactor. 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 [21]. Major drawback is requirement of pure oxygen and generation of more CO_2 than steam reforming.

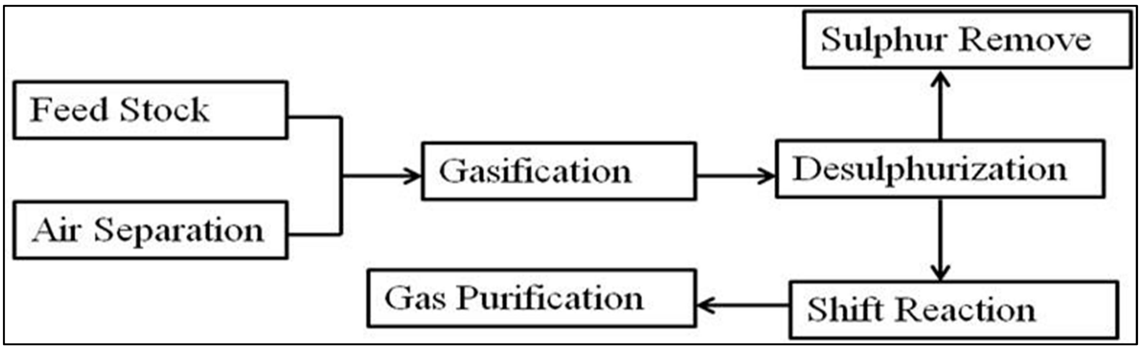

Fig 1.4: Flow diagram of partial oxidation process.

(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 Eqn. 1.6[22, 23]:

$$C_nH_m + \frac{n}{2}H_2O + \frac{n}{4}O_2 \rightarrow nCO + \left(\frac{m}{2} + \frac{n}{2}\right)H_2 \quad (1.6)$$

In Fig. 1.5, a simplified flow diagram of the OSR is available is presented. Optimal operating conditions for OSR are 700 - 800° C temperature, 0.7-1.0 O/C (oxygen to carbon) ratio and 1.5 - 2.0 S/C (steam to carbon) ratios. Transition metals are known to be an active catalyst for OSR. Most metals that are active for SR and POX individually are also active for OSR [24]. Cost of this technology is high due to Oxygen separation.

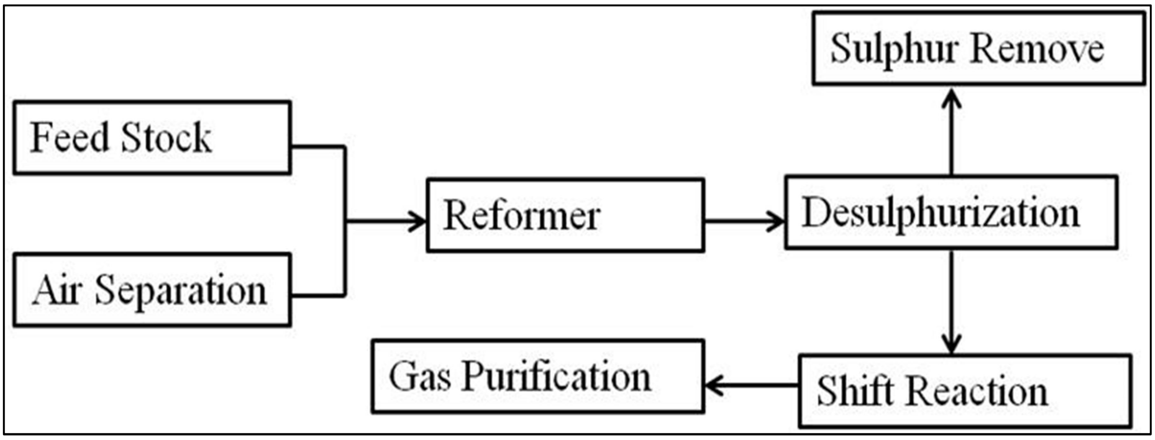

Fig 1.5: Flow diagram of oxidative steam reforming.

1.4 Solar Hydrogen

Solar hydrogen production is a key target for the development of alternative future energy system that will provide a clean and affordable energy supply. Moreover, it is carbon free and also renewable hydrogen production. Dissociation of water is not spontaneous process because $\Delta G(H_2O \rightarrow \frac{1}{2}O_2 + H_2 \quad 237\ kJ/mol)$ is positive. Therefore, energy is to be supplied which can be solar energy.

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

There are four different technologies being studied for solar hydrogen as given below:

- Photovoltaic cell plus electrolyzer,
- Photocatalytic Process,
- The Photobiological (PB) water splitting and
- The Photoelectrochemical (PEC) system that uses photoelectrode

1.4.1 Photovoltaic cell plus electrolyzer

In the Photovoltaic cell, PV panel receives solar radiation and are converted into electricity. The electricity produced by PV panel is utilized for electrolysis of water to produce solar hydrogen. Direct current is passed through water to generate hydrogen to conduct electrolysis [25].

$$2H_2O + Electrical\,energy \rightarrow 2H_2 + O_2 \qquad (1.7)$$

A PV cell is composed of semiconducting material that makes p-n junction and capable to converting light into electricity. When solar light falls on PV cell, light is absorb by a semiconductor, photons of light can transfer their energy to electrons, allowing the electrons to flow through the material as electric current. This current flow out of the semiconductor to metal contact and then it is used for dissociation of water.

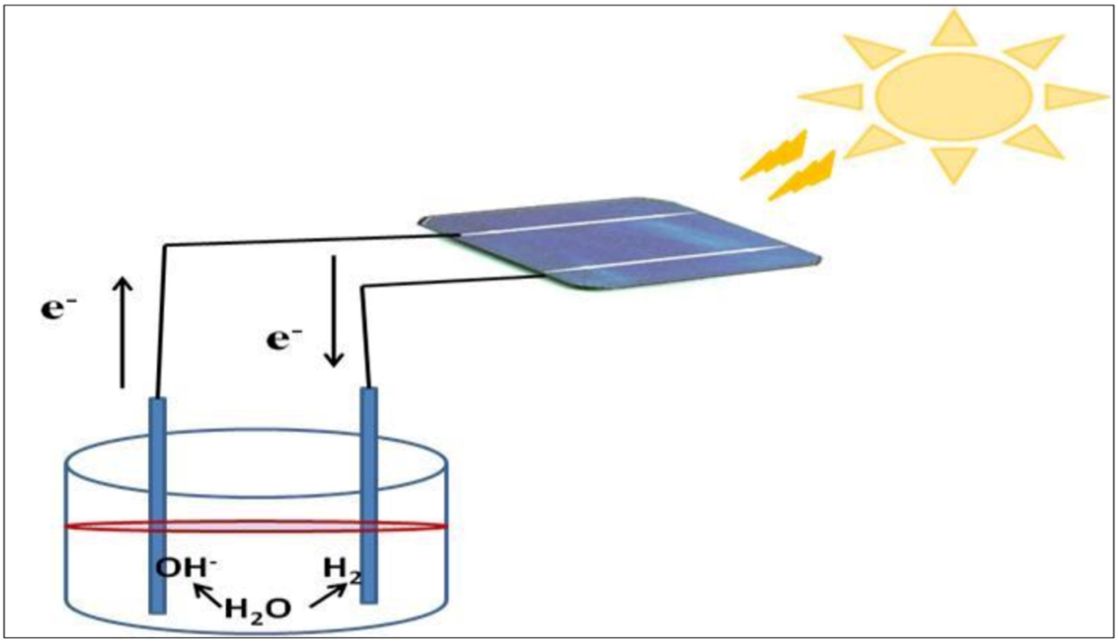

Fig 1.6 Schematic Diagram for dissociation of water by PV cell

1.4.2 Photocatalytic Process

Photocatalytic process is another technology by which water can dissociate into hydrogen. Photocatalytic process is the simplest techniques for water splitting in which each catalyst particle acts as microphotoelectrode that perform both oxidation and reduction reaction of water on catalyst surface. However, separation of charge carriers is not as efficient as with a photoelectrode system, and there are difficulties associated with the effective separation of the stoichiometric mixture of oxygen and hydrogen to avoid backward reaction [26]

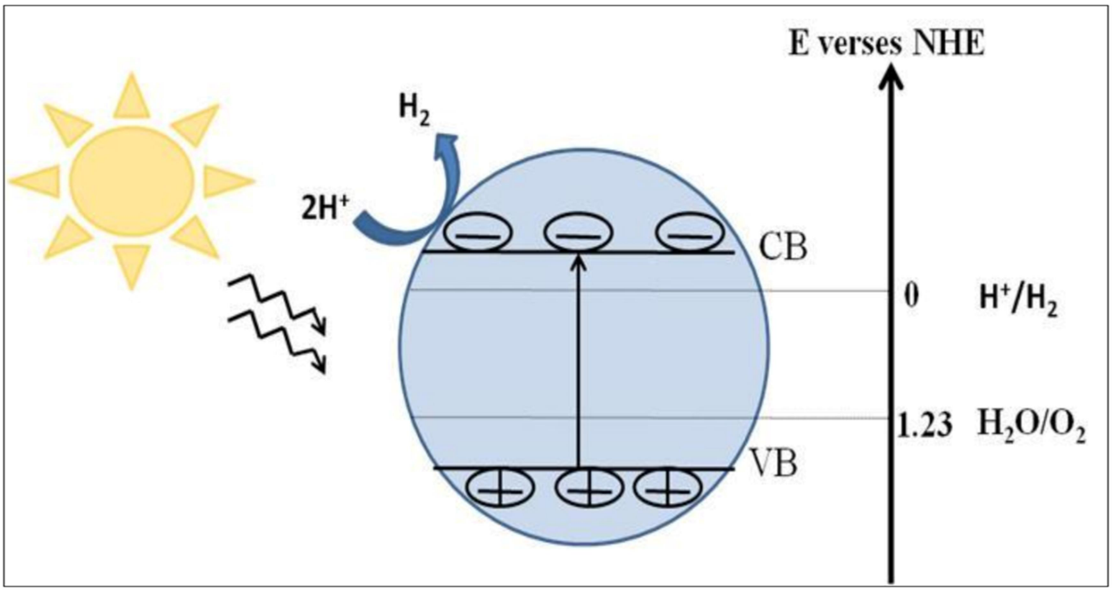

Fig 1.7 Schematic Diagram for dissociation of water by Photocatalytic process

1.4.3 The Photobiological (PB) water splitting

In photolytic biological systems, microorganisms—such as green microalgae or cyanobacteria use sunlight to split water into oxygen and hydrogen ions. Hydrogen ions can be combined through direct or indirect routes and release hydrogen gas[27]. Process for hydrogen production by photobiological process is shown in Figure 1.8. Challenges for this pathway include low rates of hydrogen production and the fact that splitting water also produces oxygen, which quickly inhibits the hydrogen production reaction and can be a safety issue when mixed with hydrogen in certain concentrations[28, 29].

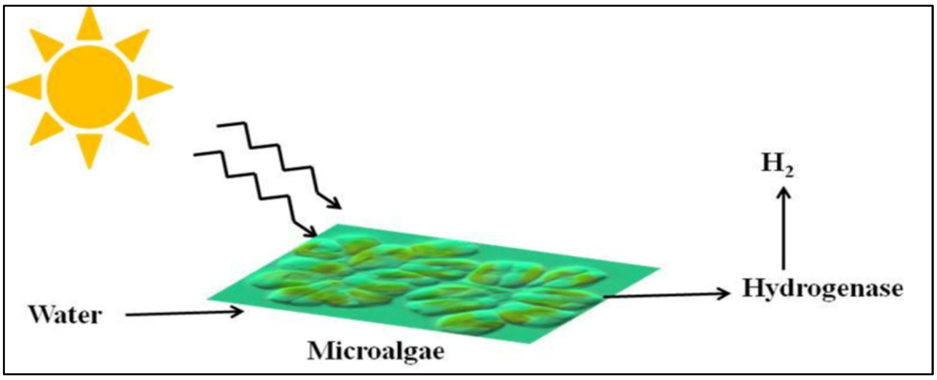

Fig 1.8 Schematic Diagram for dissociation of water by Photobiological process

However, Nagy et al [30] proposed that [Fe-Fe] type hydrogenases of green algae are very active for enhancing the hydrogen production rate.

1.4.4 Photoelectrochemical Process

Whenever at least one of the electrodes is photo responsive, electrochemical cell is called Photoelectrochemical (PEC) cell. So, PEC cell is defined as an electrochemical cell that can convert light energy into a more useful energy product through light-induced electrochemical processes. In PEC cells, water splits into hydrogen and oxygen with the aid of photoelectrocatalyst, which absorbs the photon energy and converts it to electrochemical energy as shown in Fig 1.9 This is one of the most prominent ways of producing clean and cost-effective hydrogen by taking into account all photons that continuously strike the earth's surface. The process of splitting water with the aid of electrical energy is called electrolysis of water and if it is aided by photon energy of sunlight it is called photoelectrocatalysis of water splitting. PEC water splitting utilizes both solar and electrical energy to split water into H_2 and O_2[31]. PEC water splitting is highly preferred and is a promising field of study for many research communities, because only a small biasing current is required to run the process. Since, electrolysis alone accounts for a lot of electrical energy to meet the thermodynamic potential for splitting water molecule. However, PEC water splitting requires an external energy input as per thermodynamic splitting of water splitting reaction [32].

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \qquad 237\ \text{kJ/mol}$$

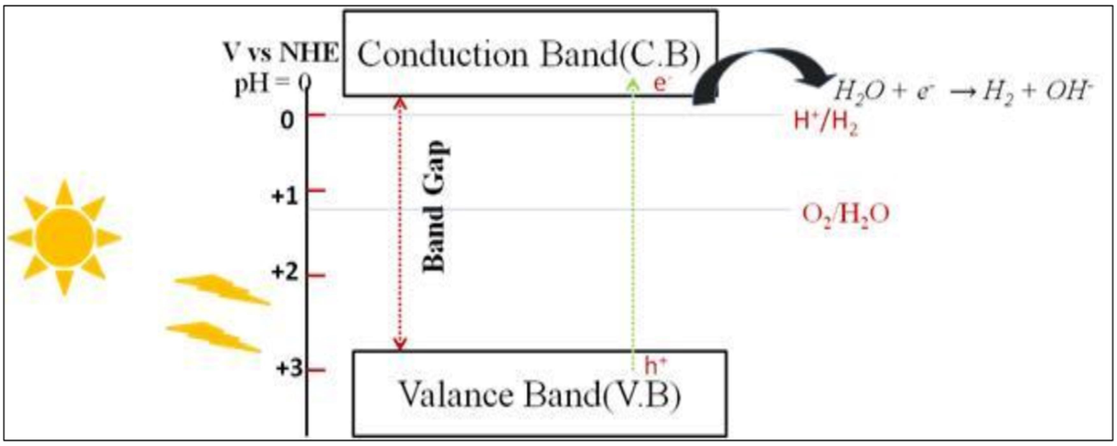

Fig 1.9 Band structure for water splitting reaction

The PEC cell consists of a working electrode (called as photoanode or photocathode) and counter electrode (usually Pt) in an electrolyte solution of water. Working electrode is excited by photon energy and generates electron and hole - pair. These photo-induced electrons reduce water/H^+ to form H_2 at Pt electrode whereas photo-generated holes oxidize water/OH^- to form O_2 at photoanodes under the influence of applied external bias. In principle, the redox potentials of photo-generated electrons and holes should be suitable for performing the redox reactions of water splitting reaction (i.e., oxygen evolution reaction, OER and hydrogen evolution reaction, HER). Since, the thermodynamic potential for water splitting reaction is 1.23V[33], the anodic and cathodic reactions will proceed only if the band edges are staggered appropriately with respect to water redox potentials

There are three steps involved in PEC water splitting reaction: (1) Charge carriers generated after absorption of photon energy, (2) charge carriers separation, and (3) migration toward surface reaction sites to perform water redox reaction. [36].