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A Review on Solar Hydrogen Production Techniques

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ABSTRACT

Solar Hydrogen economy is analyzed as a possible solution to the looming energy crisis. The present and future energy needsare projected and solar hydrogen potential to meet these needs are evaluated. Different solar hydrogen production techniques are classified according to the process involved (thermochemical, electrochemical and photochemical). Salient points on these methods are mentioned. An economic assessment of a conceivable solar hydrogen economy is also performed. PV water electrolysis along with hybrid technologies like solar methane reforming and solar cracking are suggested as a good short to midterm solution. Photocatalytic production is predicted as a possible long term solution.It is observed that most of the processes have not been extensively researched upon and promising thrust area for further research are recommended.

1. Introduction

Conventional energy sources are diminishing at an alarming rate and thus, it is a must that alternate energy sources are developed and utilized. Nuclear, wind, hydroelectric, geothermal and solar are all greener sources of energy.

Accidents related to nuclear power plants has not helped its cause in the eyes of the public.[1] It also faces challenges in waste disposal. Hydroelectric and geothermal energy sources are limited by their availability. Wind energy is a viable alternative and is being heavily researched upon. But, it also has some major drawbacks like unpredictability of wind, large area requirement and noise production. On the other hand, solar energy issafe, easily available and unlimited source of energy. Solar energy can be intermittent depending upon the availability of sunlight on earth's surface. Energy generated can be stored in form hydrogen and can be used when needed. This a desirable solution the intermittency problem.[2,3,4,5]

In this review, the amount of hydrogen required to meet the needs of the current market and the potential to produce the required amount of hydrogen using solar energy is discussed. A lot of literature is available on different solar hydrogen production techniques.[3,4,6,7,8,9,10] Categorization of these techniques isambiguous and all the methods have not been discussed in any single literature. An effort has been made to include all the solar hydrogen production techniques and classify them according to the process used: thermochemical, electrochemical and photochemical. An economic analysis of a possible solar hydrogen economy is also examined. Finally, some of the conclusions are listed and avenues for further research are also suggested.

2.Hydrogen Producing Potential of Solar Energy

Solar energy can be used to produce hydrogen in two ways. They can either be used personally or for mass production.

According to an analysis performed by Singliar[11] on Honda FCX assuming an average distance of 12,000 km/year, annual hydrogen consumption will be 140 kg. Honda has developed a "Solar Hydrogen Station" which produces 0.5 kg of hydrogen per day.[12] This amounts to 180.5 kg of hydrogen per year, easily satisfying the need of a personal fuel cell vehicle.

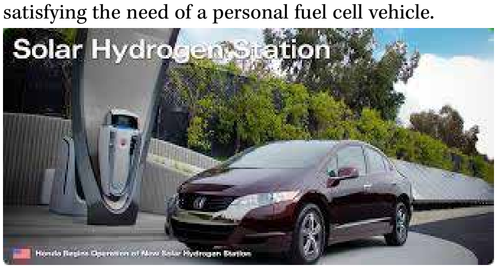

Figure 1: Solar Hydrogen Station [12]

The United States consumes an average 128 billion gallons of gasoline per year. [13] According to a study by Levene et al. [14],1110 billion kg of hydrogen can be produced using solar and wind energy. Assuming 1 kg of hydrogen is equal to 1 gallon of gasolinein energy content, hydrogen potential is 8.7 times the required amount. Even though, separate calculations are not available for solar and wind energy, solar energy alone can satisfy the hydrogen production need. Hydrogen production potential from solar energy is shown in Figure 2.

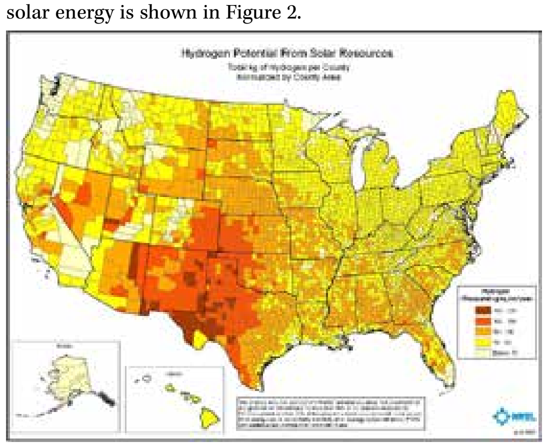

Figure 2: Total kg of hydrogen per county, normalized by the county area [14]

3.Solar Hydrogen Production Techniques

3.1Thermochemical Process

Thermochemical Processes can be further classified into two categories depending upon the number of intermediate steps involved. All thermochemical processes are shown in Figure 3.

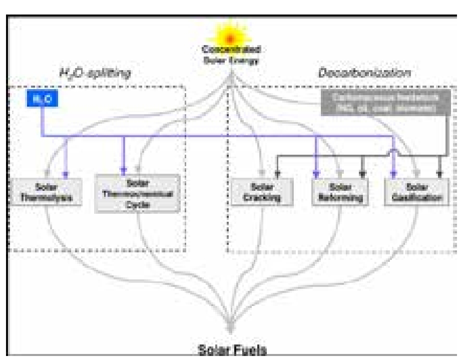

Figure 3: Thermochemical Processes for Hydrogen Production [10]

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3.1.1Direct Conversion

Solar Thermolysis is a single step process in which water molecules are directly split into hydrogen and oxygen. This is possible as water breaks down into its constituents when temperatures greater than 2000 ^{0}C are achieved. [5]

$$2\ H_2O \rightarrow 2H_2 + O_2$$

This is a highly endothermic reaction and a high temperature heat source of about 2300 ^{0} C is required.Hence, making it unsuitable from an engineering point of view. Many ideas have been proposed but they fail when severe thermal shocks are generated due to high flux solar irradiation. It is also difficult to separate the products (H_2 and O_2). [10]

3.1.2 Indirect Conversion

Indirect conversion takes place at relatively lower temperatures. It uses intermediate steps in order to avoid very high temperatures. It can be used in two ways: splitting water molecules or decarburization of fossil fuels.

3.1.2.1 Thermochemical Cycles

There are over 300 thermochemical cycles available that separate water into hydrogen and oxygen using multiple steps. It does not face the high temperate or the product separation problem.[8] An efficient two step thermochemical cycle uses the following metal oxide reactions.

Step 1(solar): $M_xO_y \rightarrow x\ M + (y/2)\ O_2$

Step 2(non-solar): $x\ M + y\ 2\ H2O \rightarrow M_xO_y + y\ H_2$

In the first step, thermal disassociation of metal takes place in the endothermic reaction. In the second step, the activated metal is oxidized to produce the corresponding metal oxide and hydrogen.[10] An example of such a process is shown in Figure 4.

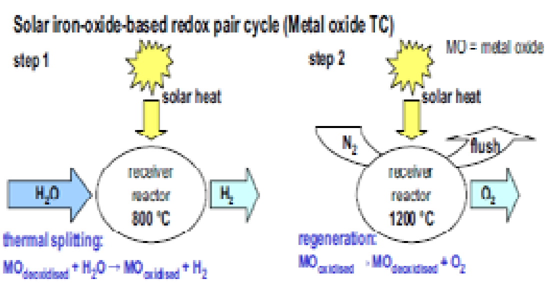

Figure 4: Two-step Thermochemical Cycle [10]

3.1.2.2Decarburization of fossil fuels

Solar cracking and solar reforming are two methods using which hydrogen can be produced from fossil fuels. Solar cracking is the thermal decomposition of fossil fuels in an oxygen free environment as explained by the following reaction.

$$CxHy \rightarrow x\ C + (y/2)\ H2$$

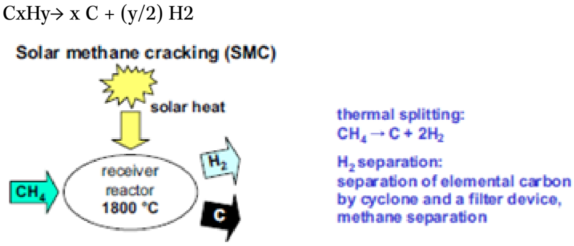

Figure 5: Solar Cracking of Methane [10]

Solar reforming it the thermal decomposition of hydrocarbon and steam at temperatures about 1000 ^{0}C. It can be expressed by the following reaction.

$$C_xH_y + x\ H_2O \rightarrow (y/2 + x)\ H_2 + x\ CO$$

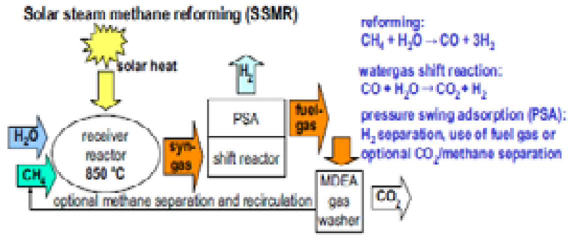

Figure 6: Solar Reforming of Methane [10]

3.2 Electrochemical Process

In this process, electricity required for splitting the water molecule is derived directly from photovoltaic panels. It can be thought of a reverse PEMFC with the required electricity being directly provided by the PV panels breaking distilled water into hydrogen and oxygen. Such a system is commonly used with an electrolyzer and the overall efficiency is below 16%. [15,16] It has been suggested that efficiency of such a system can be improved if new materials accommodating more solar irradiation are used. [5]

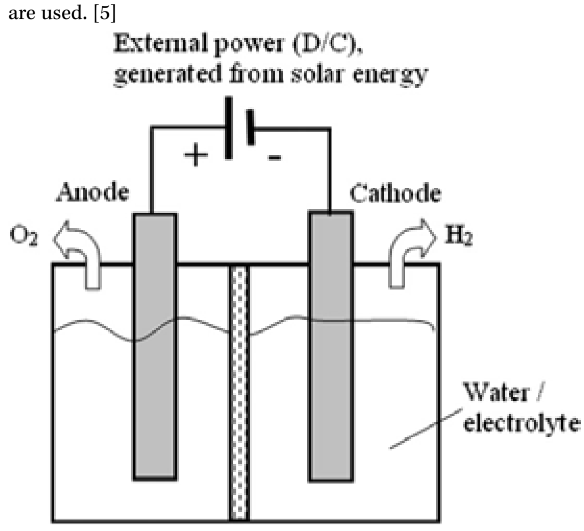

Figure 7: Electrochemical Process [5]

3.3 Photochemical Process

Photochemical processes use solar light as energy to produce hydrogen. They are of many types like photoelectrochemical, photo biological, photocatalytic, photodissociation, photodecomposition and photolysis. We will be discussing photoelectrochemical, photocatalytic and photobiological in detail.

3.3.1 Photoelectrochemical Process

This process combines solar PV and electrolysis in a single device, thereby increasing the efficiency of the system. It consists of a photoactive electrode that absorbs solar energy. When enough energy is absorbed, an electron is released producing electricity in the external circuit.[6] This electricity is used in disassociation of water molecules.

$$2\ h\nu + H_{2O \rightarrow (1/2)\ O2 + H2}$$

Where h is the Planck's constant and ν is the frequency. [8]

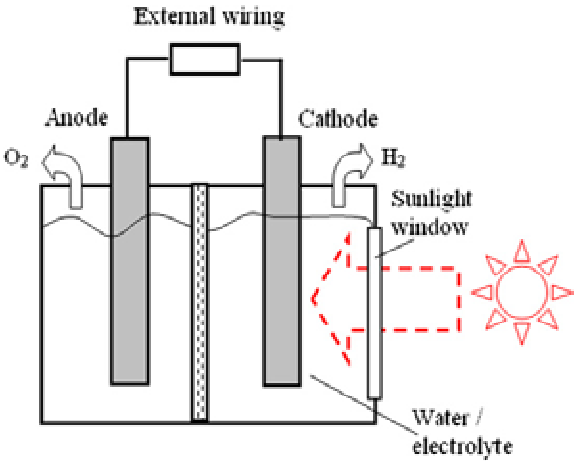

Figure 8: Photoelectrochemical Process [5]

3.3.2Photocatalytic Process

It uses a sensitizer that absorbs solar energy and uses it to activate the electrons in the valence shell of the oxygen atom in the water molecule. A catalyst is used to accumulate these electrons and uses them for oxidation of metal, producing hydrogen as a product. Chemical reactions used in this process are as follows. [5]

$4\,S + 4\,h\Upsilon = 4\,S^*$
$4\,S^* + 4\,C_R = 4\,S^* + 4\,(C_{R-})^*$
$4\,(C_{R-})^* + 4\,H^* = 4C_R + 4\,H^*$
$4\,S^* + 4\,C_{OX} = 4\,S + 4\,C_{OX+}$
$COX^+ + 2\,H_2O = 4\,C_{ox} + 2\,O^* + 4\,H^*$
$4H^* = 2\,H_2$
$2\,O^* = O_2$

Where h is the Planck's constant, Υ is the photon frequency, S is the sensitizer and CR and COX are the catalysts for reduction and oxidation reactions respectively.

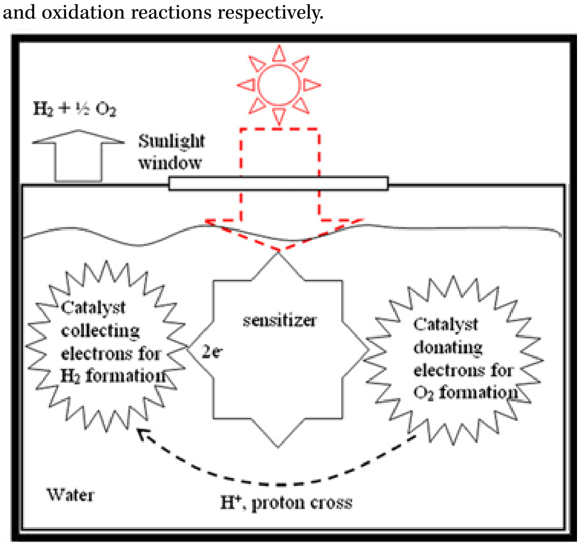

Figure 9: Photocatalytic Process [5]

3.3.3 Photobiological Process

This process is similar to photosynthesis. Light energy is used by different organisms like green algae, cyanobacteria etc. acting as catalysts to produce hydrogen along with other by products. Direct conversion is possible when high intensity of light is available. But, in this case, the photochemical efficiency is low. Indirect conversion involves multiple intermediate steps and is possible at lower luminous intensities. However, the gas mixture produced is difficult to separate.[9]

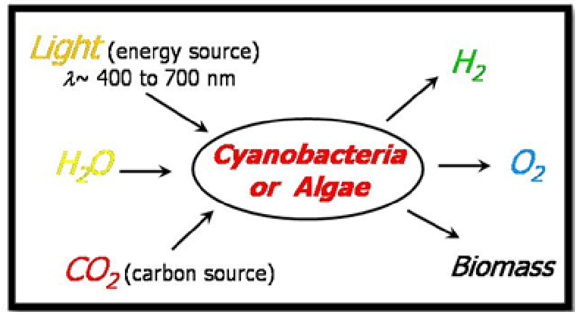

Figure 10: Photobiological Process [17]

4. Economics of Solar Hydrogen

In order to become competitive with fossil fuels in the short term and with other alternate energy sources in the long term, it is not efficiency but economics that plays the primary role.

PV water electrolysis is the most mature solar hydrogen production technology today. According to National Research Council (NRC), USA the cost of hydrogen production using this technique in 2004 was $28.19/kg of H_2producing electricity at the cost of $0.32/kWh.[18] It was further estimated that hydrogen production costs will decrease to $6.18/kg of H2and consequently electricity costs will decrease to $0.1/kWh. This is a very attractive prediction, but it has not been realized as of yet. [4,11]

ZnO/Zn thermochemical cycle was the subject of analysis by U.S. Department of Energy (DOE) in 2011.[19] They set targets for the gallon of gas equivalent price of hydrogen for 2015 and 2025. Target price for 2015 is $6/gge and for 2025 is $3/gge. They assume an efficiency of 30% and 35% in 2015 and 2025 respectively. The efficiency today is below 10% and achieving the aforementioned target within the given time frame seems highly unlikely. [20]

Using concentrated solar radiation to produce high temperature can work at 21% efficiency, providing hydrogen at $2.8/kg.[21] At present, the cheapest thermochemical process to produce hydrogen is through solar methane reforming and solar methane cracking.[22] But, as the price of fossil fuel rises, solar metal oxide cycles (especially sulfur-iodine cycles) should become competitive economically.

5. Conclusions and Avenues for Further Research

It is inevitable that fossil fuels will be replaced by cleaner and greener sources of energy in the future. Solar hydrogen provides a very lucrative solution to the impending energy crisis.

The major limitations of a solar hydrogen economy is high cost, as none of the technology available today is anywhere near economic viability.[4] A lot of research is already going on in this field and the future does look promising.

In order to integrate solar hydrogen to the current industrial needs, hybrid processes should be researched upon as a short to midterm solution. This will help in obtaining more research grants as immediate needs will be met and the technology will also grow hand in hand. Eventually, a complete transformation to solar hydrogen economy should be aimed at.

PV water electrolysis is the most mature of the solar hydrogen production technologies. It has also been shown to be economically feasible for remote locations.[6,16,23,24] Its chief drawback is high cost and that is due to high solar plate cost and low electrolyzer efficiency. Work is already being done on both of these areas and the results being obtained are encouraging. [25]

Use of collectors that track the sun will increase the efficiency of a PV system. It has also been claimed that pointing the collector towards sky will increase the efficiency by 40% compared to pointing it towards the obscured Sun.[26] This is an interesting idea but no experimental data was given to back up the hypothesis and a comparative analysis is required before bringing it into practice.

Materials used in PV systems are not always compatible with those used photoelectrochemical processes. Hence, a database of materials along with their properties should be developed for this process.

Regulation of codes and standards are important to the growth of any technology. Hydrogen storage and transport have progressed a lot in the past few years and standards for most applications are available.[27] Similarly, a guideline for manufacture of parts used in solar hydrogen production should also be established.

Photocatalytic production of hydrogen is in its nascent state and it is already being touted as a long term solution.[4] In order to make it competitive, additional research on semi-conductors suitable to this process should be conducted.

There are many thermochemical cycles available for hydrogen production. Even though they work at high efficiencies, the high temperatures required is an issue from material science point of view. ZnO/Zn is a likely process that can become economically viable in the near future.[19] But, before that it faces a lot of technical challenges and R&D effort should be concentrated in this region.

It is not only the production techniques, but the storage, distribution and auxiliary components that add to the cost of hydrogen.[5] In order to achieve the dream of a hydrogen economy, efforts should be made bring down the overall cost.

Going through the literature, it was observed that the economic forecasts greatly vary. It is obvious that fluctuation of price is very difficult to predict and thus, it becomes tough to envisage a time frame for the imminent hydrogen economy. Looking at the work being done in this area and the rising cost of fossil fuels it only seems a matter of time before the world turns to a hydrogen based economy.

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