Review and Assessment of Hydrogen Production Methods for Alternative Fuel and Better Sustainability

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Abstract-*Due to rising use of automobiles and other automotive machines, the fossil fuel consumption is increasing rapidly. The fossil fuel reservoirs, hence, are under great stress and the scenario is likelier to aggravate than mitigate. The need to discover alternate fuel is evident more than ever. Hence, hydrogen, as an alternative fuel, has attracted a lot of attention from both academic and industrial sector. It is recognized as the most important element of next generation clean energy technology. The first step towards achieving this is production of hydrogen. Ever since the first method of hydrogen production i.e. dissolving iron in acid vitriol was introduced (in 15th century), timely upgrades have been made to make hydrogen production practically feasible and cost effective. In this review, we attempt to list out various methods of hydrogen production, classify them according to their fundamentals, provide the description and review the results obtained after performing those methods. We explain the potential of each method, difficulties involved in that method, proposed solutions and the practical efficiency of each method, supported by authentic results*

Keywords*-* Direct Electrolysis, Hydrogen Production, Steam Reforming, Thermolysis

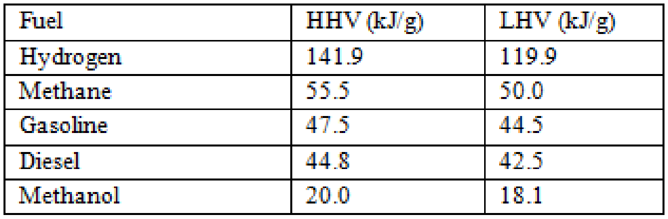
I. INTRODUCTION

Population in twenty first century is soaring high and hence, the resultant increase in energy demand has become tough to cope up with For instance, in 2011, 15 TW energy was consumed by approximately seven billion people world-wide. By 2050, these numbers are expected to escalate to 30 TW and nine billionpeople, respectively [1]. 85% of the global energy supply was met by fossil fuels in 2011. But, fossil fuels are not probable to keep up with the increase in energy demand due to their limited reserves and uneven distribution. Also, fossil fuel sites have become less accessible over the period of time and hence stress on easily accessible ones has increased leading to political and economical issues. Along with these, the global warming caused by fossil fuels is also quite alarming and soon needs to stop. Thus, switching to alternative fuels that do not emit CO_2 has become indispensable.

With near-zero or zero end use emissions and continually replenished sources, hydrogen can be an ideal sustainable energy carrier. [2]. In order to remove the adverse effects offossil fuel utilization on the environment, human health,and the climate, hydrogen should be produced from cleanand abundant sources with environmentally benignmethods [3,4]. This concept is called as “green hydrogenproduction”.Green hydrogen technologies are not quickly accessiblewith sensible effectiveness and expense. For instance,studies on effectiveness and cost of PV electrolysis for largeand small scale hydrogen production show that PV electrolysisis currently expensive (>$5/kg for H2) and it cannot reachhigh conversion efficiencies (with energy and exergy efficienciesless than 5%) [5].Some of the advantagesof hydrogen can be listed as: (i) high energy conversionefficiencies; (ii) production from water with noemissions; (iii) abundance; (iv) different forms of storage (e.g.gaseous, liquid, or in together with metal hydrides); (v) longdistance transportation; (vi) ease of conversion to other formsof energy; (vii) higher HHV and LHV than most of the conventionalfossil fuels (Table 1). On the other hand, most of thehydrogen production methods are not mature, resulting highproduction costs and/or low efficiencies [6].

In the literature reviewed, there were several studies showing how hydrogen can be a sustainable and renewable source. [7-9]. Analysis of high temperature water dissociation,thermochemical water splitting, water electrolysis, andphotolysis has been conducted by Lodhi [10], which isconsidered as one of the early works. Later, Lodhi [11]classifiedsolar, sea/ocean, hydro, wind, and nuclear energy asgreen primary sources to produce hydrogen. In Ref. [11],green material sources to generate hydrogen are listed asfresh and sea water, hydrogen sulfide, and biomass.Hydrogen production methods can be classified as “green”based on their primary energy source and/or the material hydrogen is extracted from Ref. [12]. Cost assessment of centralized and distributed hydrogen production and transportation issues (i.e. compression, distribution, and storage)are studied by Lemus and Duart [13].Hydrogen can also be produced by mimicking photosynthesisreactions. These methods are summarized byAlstrum-Acevedo et al. [14] Catalytic hydrogen production methods from biomass (i.e. gasification, pyrolysis, and sugarconversion are reviewed by Tanksale et al [15]. Acar andDincer [6]presented a comparative cost, environmentalimpact, and technical assessment of natural gas steam reforming, coal gasification, water electrolysis via wind and solar energies, biomass gasification, thermochemical watersplitting with a CueCl and SeI cycles, and high temperatureelectrolysis.

Table 1: Higher and lower heating values of hydrogen and common fossil fuels at 25˚C and 1 atm. [16]



Fuel	HHV (kJ/g)	LHV (kJ/g)
Hydrogen	141.9	119.9
Methane	55.5	50.0
Gasoline	47.5	44.5
Diesel	44.8	42.5
Methanol	20.0	18.1

II. HYDROGEN PRODUCTION

There are several different methods to produce hydrogen and each method fundamentally differs from other on basis of its energy source, method implemented and nature of mechanism. These methods are primarily classified as hydrogen produced from primary energy sources and that from secondary ones. Primary energy sources include nonrenewable energy sources like fossil fuels and renewable ones like solar energy, wind energy and biomass. Another way of classifying hydrogen production methods can be sorting it out on the basis of raw material utilized. These include, hydrogen production by the direct reaction of chemical reagents including metals, acids and bases, hydrogen production from hydrocarbons including fossil fuels and biomass, hydrogen production by the direct splitting of water.

A. HYDROGEN THROUGH DIRECT REACTION OF CHEMICALS

i) Reaction of zinc and sulphuric acid.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow$$

In this reaction, zinc reacts with sulphuric acid to form zinc sulphide and hydrogen. The reaction, though it takes place in aqueous medium does not consume water. It is highly exothermic and hence care must be taken to clear off all explosives from the vicinity. This reaction mainly derives its energy from two chemicals: zinc and sulphuric acid.

ii) Reaction of silicon and sodium hydroxide:

$$2NaOH + Si + H_2O \rightarrow Na_2SiO_3 + 2H_2 \uparrow$$

This reaction uses reaction of silicon and sodium hydroxide with water to produce hydrogen. This reaction produces heat in large amount and hence, if used efficiently, this method will be quite profitable.

iii) Reaction between water and alkali metals:

$$2Li+2H_2O \rightarrow 2LiOH+H_2\uparrow$$

In this reaction Lithium reacts with water to evolve hydrogen gas and yields Lithium hydroxide as a byproduct.

$$Al+3H_2O = Al(OH)_3 +3/2H_2\uparrow$$

Reaction of aluminium can also be catgorised similarly as it also exhibits similar mechanism. Aluminium splits hydrogen to evolve Hydrogen gas and yield Aluminium hydroxide as a byproduct. But this reaction has a certain drawback as the passivation ofAluminium surface prevents further reaction. To combat this, Lang et al. used Gallium-based alloys and the results obtained showed that reactions were more effiecient after using Gallium-based alloys. The Gallium helps in sustaining the reacton for a longer period of time by creating a liquid alloy that moistens the aluminium surface and prevents passivation. Alumnium is expected as high energy carrier in upcoming hyfrogen economy but it consumes more energy and requires other energy sources too.

B. HYDROGEN FROM HYDROCARBONS

Many hydrocarbons which are used for combustion can be used in producing hydrogen. Fossil fuels require heat and catalysis to be transformed into hydrogen. The efficiency of this method is soaring high since new researches are put into effect to maximize the output. To produce hydrogen from biomass, gasification is must since biomass is not in gaseous form primarily. The efficiency of gasification and ultimately the entire production method depends on temperature and catalysts.

A. Hydrogen from Fossil Fuels

95% [17] of total hydrogen production is accountable to hydrogen production via steam reforming. Thus, you can conclude that this is the most dominating source of hydrogen production. The reason for this is its entire thermodynamic feasibility, sophisticated engineering development and high efficiency. [18] Hydrogen can be produced from fossil fuels using several other methods too, namely, partial oxidation, plasma reforming, autothermal reforming and coal gasification.

In steam reforming method, steam reacts with fossil fuels at high temperature. Other than methane; propane, gasoline, diesel fuel and ethanol can also be used in steam reforming process as these contain hydrogen in abundant amount.

The general hydrocarbon steam reforming reaction is [19]

$\mathrm{C}m\mathrm{H}n+ m\mathrm{H2O} = m\mathrm{CO}+(m+n/2)\mathrm{H}_2$

ΔH = hydrocarbon dependent, endothermic. For methanol as an example, it will be 12

$CH_3OH + H_2O = CO_2 + 3H_2$, $\Delta H = 49$ kJ mol−1

And for pure methane:13

$CH_4 + H_2O = CO + 3H_2$, $\Delta H = 206$ kJ mol−1

$CH_4 + 2H_2O = CO_2 + 4H_2$, $\Delta H = 165$ kJ mol−1

Fuel processing requires modest temperatures depending on the specific hydrocarbon as the feedstock. For example, methanol, DME (dimethylether), and other oxygenated hydrocarbons that can be readily activated at a temperature above 180 ˚C, and for most conventional hydrocarbons, the temperature should be above 500 degree C. [20-22]

In this process, typically two types of metals are used. Non-expensive metals like Nickel and expensive ones like platinum or rhodium. Between them, the less expensive nickel catalysts are used almost universally in industry because the major limiting factors with conventional steam reformer reactors are not on kinetics and the activity of the catalyst, but on the severe mass and heat transfer limitation. [23-24]

B. Hydrogen from Biomass

Biomass is the term used to describe all biologically produced matter and it is the name given to all Earth's living matter. It is a general term for material derived from growing plants or from animal manure (which is effectively a processed form of plant material). [25]. Biomass energy is derived from plant and animal material, such as wood from natural forests, waste from agricultural and forestry processes, and industrial, human or animal wastes. The stored energy in the plants and animals (that eat the plants and other animals), or the waste that they produce is called biomass energy. It is a natural process that all biomass ultimately decomposes to its molecules with the release of heat. And the combustion of biomass imitates the natural process. So the energy obtained from biomass is a form of renewable energy and it does not add carbon dioxide to the environment in contrast to the fossil fuels. [26] Of all the renewable energy sources, biomass is unique in that it is, effectively, stored solar energy. Furthermore, it is the only renewable energy source of carbon and is able to convert into convenient solid, liquid and gaseous fuels.[27]

Because of the progressive depletion of conventional fossil fuels, in recent years, the utilization of biomass energy as a renewable energy source has gained particular interest. [28] The growing interest is driven by the facts including the following ones: [29]

1) it contributes to poverty reduction in developing countries,
2) it meets energy needs at all times, without expensive conversion devices,
3) it can deliver energy in all forms that people need (liquid and gaseous fuels, heat and electricity),
4) it is CO2-neutral and can even act as carbon sinks, and
5) it helps to restore unproductive and degraded lands, increasing biodiversity, soil fertility and water retention.

Comparing to other pathways of hydrogen production, that from biomass is competitive in several ways: [30]

1) independence from oil imports,
2) net product remains within the country,
3) stable pricing level,
4) the CO2 balance can be improved by around 30%.

The production of hydrogen using biomass can be categorized into two parts: thermochemical and biological methods. Thermo chemical conversion processes such as pyrolysis, gasification, steam gasification, steam reforming of bio-oils, and supercritical water gasification which directly use bio-renewable feedstocks to produce hydrogen. [31] Biological production of hydrogen can be classified into biophotolysis of water using green algae and bluegreen algae (cyanobacteria), photo-fermentation, darkfermentation, and hybrid reactor system. [31]

Gasification of biomass generally follows the reaction:

Biomass + O_2 (or H_2O) →CO, CO_2, H_2O, H_2, CH_4+ other CH_s + tar + char + ash

This reaction is within a thermal treatment, which results in a high production of gaseous products and small quantities of char and ash. Combustion is involved in the gasification process to provide heat for theendothermic pyrolysis reactions.[32] The resulting gas after the high temperature process, is a mixture of carbon monoxide, hydrogen and methane, with carbon dioxide and nitrogen, known as producer gas altogether. [33] Having been identified as a possible system for producing renewable hydrogen, biomass gasification is beneficial to exploit biomass resources, to develop a highly efficient clean way for large-scale hydrogen production, and has less dependence on insecure fossil energy sources.[34]

C. HYDROGEN PRODUCTION BY DIRECT SPLITTING OF WATER

Theoretically, this is the most promising hydrogen production method since it has potential to produce highest output as compared to other methods. Also, another advantage is it has no harmful impact on environment. There are many different ways to carry out this particular method. Balta et al. [35] summarized the review articles on thermochemical water splitting available in the literature. One of them is electrolysis. The main disadvantage of electrolysis method is the conversion of energy from electrical to chemical. Thermolysis of water is the thermal decomposition of water at very high temperature. It uses heat as the energy source. For water alone, the temperature required (2000 ˚C to 3000 ˚C) is too high for any practical use, but catalysts can accelerate the dissociation of the water molecules at lower temperatures. Photoelectrochemical water splitting uses solar energy to split water and hence looks very promising. Some recent studies focused on the combination of different types of water splitting methods. It is extrapolated that 10% efficiency of thermal photocatalytic generation of H_2 could be achieved at approximately 400 ˚C in high pressure vessel with the help of catalysts. [36]

A. Thermolysis and Thermochemical Decomposition of Water

Thermolysis is chemical reaction in which a compound breaks into two or more substances when heated. This reaction is usually endothermic since heat is consumed for breaking the bonds. When heated to a high enough temperature, water will break up into hydrogen and oxygen. By separating the equilibrium mixture of these two generated gases, the desired pure hydrogen can be obtained.

The net reaction

$$H_2O \rightarrow H_2 + 0.5\ O_2$$

produces only hydrogen and oxygen. The experimental solar thermolysis of water study conducted by Baykara [37] achieved 90% of the equilibrium at a residence time of 1 ms and temperature of 2500 K.

However, thermodynamically, the Gibbs function (ΔG, or free energy) of the aforementioned water decomposition does not become zero until the temperature is increased to about 4700 K.38 (temperature varies with condition parameters, sometimes it is considered about 4300 K. Although, theoretically, thermodynamic balance is not a prerequisite condition for hydrogen evolution, a temperature of at least 2100˚C must be maintained in the reactor to make the process economically feasible. [38] And to maintain such a high in-reactor temperature, the inner structural component of the reactor should at least resist a temperature of 2300˚C. It makes the selection of reactor materials and the separations of the two gases extremely difficult. Even at about 2200˚C, most non-oxide refractory materials are already unstable, and H_2 is expected to have a reactive effect on oxides at these extremely high temperatures. [39] Besides, the consumption of energy in the process increases dramatically with the required temperature because of the huge radiation losses at such temperatures. All these problems make direct splitting a very difficult process and hence, it is carried out in stages. Such a process is termed a “thermochemical water splitting cycle,” and the function of chemical reactants within the cycle can be considered as that of catalysts. In these cycles, the decomposition temperature requirement is represented by that of the endothermic “high-temperature step,” which is followed by one or more exothermic “low-temperature” reaction steps. The temperature requirement in the “high temperature step” (700 ˚C–2000 ˚C) [40] is considerably lower than in direct thermal water splitting. The previously mentioned difficulties on energy losses and reactor materials under high temperature arelargely reduced, giving a higher efficiency and a wider range of material selection. To avoid occurrence of any problem due to intermediate losses, it is idea to have cycles with opportunities for energy recovery. It is also of utmost importance to check that all the chemicals and reagents utilized in process are recycled and reused. Otherwise, the prime advantage of thermolysis i.e. water being the only net reaction will be annulled and sustainability and renewability will be chipped away.

More than 400 cycles were considered possible for thermochemical hydrogen evaluation by the US Department of Energy. Among this large pool, researchers evaluated and chose nine technically and practically feasible candidates. [40] Two intensely studied cycles as the representatives of them are those of Zn/ZnO and FeO/Fe_3O_4.[41-42] Their advantages include:

1) They have only two steps, making the energy losses between steps minimized and the whole procedure relatively simple;
2) Hydrogen and oxygen are obtained in separate steps, leaving little hazard of explosion from their mixture.
3) Clear-cut circulation of steps requiring and not requiring solar energy makes both day-time with sunlight and night-time without sunlight well used. In these reactions, usually, more multifaceted catalytic or electrolytic chemicals are used instead of metal oxide. As the result of the change of catalytic system, the exothermic steps often involve more procedures or more electrochemical operations. [44] The superiority of this type of cycles over their counterparts of high temperature cycles is that their reactions typically require an operation temperature below 1100 ˚C, which is considerably lower than those of high temperature cycles. However, at the cost of the greatly reduced operation temperature, these cycles involve more steps therefore more chances of energy losses and much more processing complexity.

B. Direct Electrolysis of Water

Electrolysis of water to produce hydrogen is a comparatively simple and efficient way among most methods. It already has a history of more than 200 years. [45] Around four percent of hydrogen gas produced worldwide is still created by electrolysis. This splitting of water can be achieved through directelectrolysis or via one of the several thermochemical cycles where the net reaction is the decomposition of water. Thermochemical cycles aim to avoid the Carnot efficiency limitations in the production of electricity from thermal energy, and thus can potentially have higher efficiency than the electrolytic process [12]. However, this higher potential efficiency may not be realized because of the complexity and poor selectivity of the proposed thermochemical systems. As a result, the electrolytic decomposition of water, a relatively well-known and established technology, may possibly be superior to any thermochemical cycle [13-14]. Electrolysis of water can be conducted in conventional or advanced alkaline electrolyzers, solid-polymer electrolyzers, or high-temperature, water-vapor electrolyzers. [46] Each of these configurations uses electrical energy to split water into hydrogen and oxygen in an electrochemical cell consisting of an anode, a cathode, and an electrolyte. Hydrogen is formed at the cathode and oxygen at the anode. Due to their high turnover rates, homogeneous catalysts are less expensive than the heterogeneous ones. In the literature, there are some homogeneous catalysts with turnover rates of 2.4 mol of hydrogen per mole of catalyst and second [46]. Since electrolyzers (especially PEM electrolyzers) are highlysensitive to the purity of water, desalination and demineralizationmust be applied before electrolysis process. One of the method is utilization of ion-selective membranes to desalinate water. This method is proposed by El-Bassuoni et al. [47] when used as a catalyst, magnesium supports oxygen evolution reaction instead of chlorine generation. [48] The differences between electrolysis systems involve the operating temperatures, electrolyte properties, and to some degree, the operating pressures. The high-temperature electrolysis (HTE) of water at 1100–1250K is typicallyaccomplished using yttria-stabilized zirconia (YSZ) as an electrolyte [47]

The reactions occurring in a HTE process are shown below [48]:

Cathode: H2O + $2e^- \rightarrow H_2 + O^{2-}$

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

HTE cells are either in a tubular form or in planar stacks [12, 49]. The primary components are the anode, cathode,electrolyte, and interconnect material. A common anode material is strontium-doped lanthanum-manganite. The cathode is typically a nickel–zirconia cermet. The electrolyte is yttria-stabilized zirconia. The interconnects are ferriticstainless steel. The cell voltage and the current density in HTE are typically 0.95–1.3V and 0.3–1.0A/cm2, respectively. [47] The HTE process has thermodynamic (lower voltage) and kinetic (high current density) advantages over other processes. However, the high temperature process engineering and materials of construction are developmental issues that need to be addressed before the technology can be commercialized [50].

The standard potential of electrolyzing pure water into hydrogen can be calculated thermodynamically. At 1 bar and 25˚C, the Gibbs free energy ΔG of the water splitting reaction is 237.178 kJ/mol.51 From chemical kinetics, the thermodynamic reversible potential. [51]

$E = V\text{rev} = \Delta G/n\text{F} = 1.23\ \text{V}$

Where n is the moles of electrons and F is the Faraday constant.

At this voltage, the reaction is endothermic because of the change of entropy ΔS. Taking the thermal factor into account, when no heat is absorbed or generated, the electrical energy is equal to the enthalpy $\Delta H = \Delta G+T\Delta S$ = 28583 KJ/mol at standard condition. Therefore the thermoneutral voltage can be calculated as

Vtn= $\Delta H/$nF= 1.48 V

The electricity used in the electrolysis for hydrogen production could be generated from energy resources including nuclear, wind, solar and bioenergy. Among these resources, solar, especially solar photovoltaic energy, [52] possesses many special attributes and is the only renewable resource which could actually meet the predicted demand of the middle of this century55 (while nuclear energy being the only nonrenewable resource).

C. PV Electrolysis

The photocatalysis converts photonic energy (comes from solar irradiation) to chemical energy (hydrogen). The energy carried by the photon is proportional to the frequency of the radiation and given by hn where h is the Planck constant and n is the frequency. When a photon hits the photocatalyst, an electron-hole pair is generated and the obtained electrical charge is utilized to dissociate water. Acar et al. [53]reviewed and assessed various simple and complex photocatalystsbased on their H2 production yield, efficiency, andimpact on human health and the environment. The photoreductionand photo oxidation reactions can be written as.

Photo reduction : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Photo oxidation : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Here, photoelectrochemical cells (PEC) convert solar energy to an energy carrier via light stimulated electrochemical processes. In a PEC, solar light is absorbed by one or both of the photoelectrodes and at least one of them is a semiconductor. PECs can produce either chemical or electrical energy. They are also used to treat hazardous aqueous wastes [54] the cost of hydrogen from PV electrolysisis about 25 times higher than that of fossil fuel alternatives However, the cost of this process has been continuously decreasing and this factor is estimated to go down to 6 [55]. Considered as the most efficient renewable method of hydrogen production, [51]interests are widely shown world-widely by researchers aiming at making hydrogen as a clean and sustainable energy source. Several researches were carried out on this particular technology to squeeze out best possible results from it.

D. Photoelectrolysis:

As mentioned in previous paragraphs, electrolysis of water always transforms electrical energy into hydrogen-carried chemical energy. As a result, whether the hydrogen production is renewable depends on where the electrical energy is from. Obviously, using electricity from fossil fuels will hardly make the energy cycle sustainable. Only processes based on renewable energy sources could be considered. One widely accepted route is to firstly collect solar energy and convert them into electrical energy, and then to electrolyze water with the energy collected.54 The photoelectrolytic hydrogen production mechanism includes the following steps: (i) generation of an electron-hole pair with the help of a photon that has sufficiently high energy (higher than the band gap of the pen junction), (ii) flow of electrons from the anode to the cathode generating electricity current, (iii) decomposition of water into hydrogen ions and gaseous oxygen, (iv) reduction of hydrogen ions at the cathode to form hydrogen in gas form, (v) separation of the product gases, processing, and storage.[59]

I. PLASMA ARC DECOMPOSITION

Plasma is an ionized state of matter which contains electrons in an excited state and atomic species. Plasma has a potential to be used as medium for high voltage electric current release due to the presence of electrically charged particles. [2] Fulcheri et al. [49] studied this reaction

$$CH_4 \rightarrow C_{(s)} + 2H_{2(g)},\ \Delta H = 74.6 \text{MJ/Kmol}$$

The setup has three electrodes connected to 3 voltages, out of which, 2 of them are introduced to Plasma gas. Their results show a 100% pure hydrogen production with zero CO_2 emissions (solid state carbon black remains at the bottom of the reactor). Plasma arc decomposition can be classified as “high temperature pyrolysis”. Gaudernack and Lynum [56] state that plasma cracking has a potential to reduce hydrogen production cost by at least 5%, compared to large scale steam methane reforming with carbon dioxide sequestration.

II. DARK FERMENTATION

Biochemical energy, which is stored in organic matter, can be used by living creatures to extract hydrogen in the absence or presence of light. Dark fermentation is the conversion of biochemical energy stored in organic matter to other forms of energy in the absence of light (this case might happen when there is reduced supply of light). The bioreactors used for dark fermentation are simpler and cheaper compared to photofermentationsince the process does not require solar inputprocessing. Hydrogen production by dark fermentation hasseveral other advantages such as the ability to producehydrogen from organic waste and therefore control and stabilizebiological waste which has a potential danger ofcontamination. For instance, dark fermentation can be integratedinto wastewater treatment systems to produce H2 fromwastewater. Producing hydrogen from organic waste has apotential to reduce hydrogen production costs since organicwaste (including wastewater) is cheap and easily available.Hydrogen production from water diluted olive oil by study byKoutrouli et al. [57]show a maximum 640 g of H2 per tonne ofolive pulp. A hydrogen production yield of around 77 g H2 perkg of glucose is reported by Das and Veziroglu [58]. Low productioncapacity per unit of (production facility) capital investmentis one of the major challenges of anaerobicdigestion. [02]

III. SUMMARY

A. Environmental Impact

As we have studied different production methods, they are now compared on the basis of key benefits, major R&D needs and critical challenges. Among all methods, the cheapest one is to produce hydrogen using natural gas. But, from long-term perspective, it’s not feasible. Optimizing capital, operating and maintenance costs as well as developing systems with high efficiencies, low impurity levels, and emissions, and increasing the role of renewable energies are some of the critical challenges of the hydrogen economy. [2] In the end, in order to have clean source of energy, Hydrogen should be produced only from methods that have no CO_2 emissions and ultimately, no harmful effect on environment. The major concerns in this sector are production quantity, efficiency, cost, system reliability and environmental impact. Thus, the carbon-free society is now not possible without hydrogen economy. This study reviews and analyses various methods, their potentials, challenges and efforts pursued in order to minimize drawbacks. These efforts help in preventing the likely inevitable energy crisis in future. Comparing the methods from environmental perspective, we first need to define Global Warming Potential (GWP) and Acidification Potential (AP). The information regarding minimizing CO_2 emissions can be found in refs [60-61]. GWP is CO_2 emissions while AP indicates SO_2 discharge on soil and into water and measures the change in degree of acidity. [62] Bhandari et al. [50] and Ozbilen et al. [62] published some results regarding GWP and AP assessment. Table presents the results of GWP and AP assessment.

B. Social cost:

Marginal external cost of a unit of CO2 emissions is identified as social cost of carbon (SCC). SCC values are estimated by using an integrated assessment (IAM) framework. First step of social cost of carbon estimation is to define thereference socio-economic scenarios which are characterizedby population, emissions, and production rate of the assessedtechnology. Climate change effect is calculated based ongreenhouse gas concentrations and temperature variations.These variations from the baseline scenario and their impacton the economy are taken as the basis of SCC calculations.Next, the baseline scenarios are marginally perturbed by theaddition or removal of amarginal unit of CO2 emissions. Socialwelfare, which depends upon consumption and the choice ofdiscounting parameters, is calculated for each baseline andmarginally perturbed scenario. The normalized difference inexpected welfare between the baseline and perturbed scenariosgives the social cost of carbon (SCC) [63].In this study, the SCC of selected hydrogen productionmethods is calculated based on the results published by Parryet al. [64]. An average of $160 per tonne of CO2 emissions isused to estimate the SCC of each hydrogen productionmethod.

C. Financial Comparison:

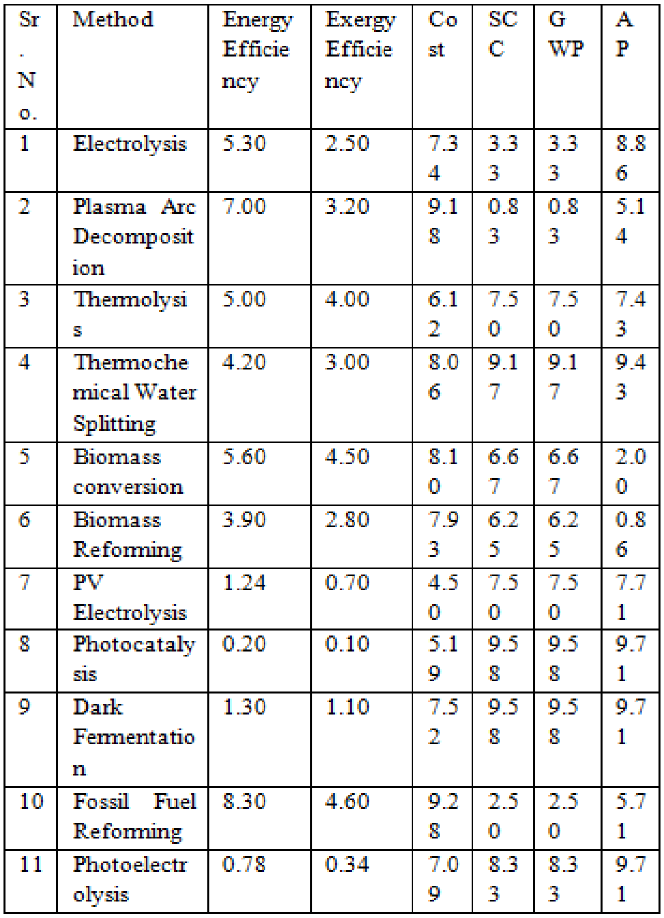
The selected methods, hydrogen production cost of water electrolysis, thermochemical water splitting, biomass gasification, photocatalysis, coal gasification, and fossil fuel reforming are taken from Parthasarathy and Narayanan [64]. Plasma arc decomposition, thermochemical biomass conversion and reforming, dark fermentation, biophotolysis, photofermentation, artificial photosynthesis, and photoelectrolysis cost data is compiled from Uddina et al. [65]. Thermolysis, PV electrolysis, high temperature electrolysis, and hybrid thermochemical cycles’ hydrogen production cost data are obtained from Ngoha and Njomo [66]. And the hydrogen production cost of photoelectrochemical method is attained from Trainham et al. [67]. According Table 2, the most financially advantageous methods for hydrogen production are steam methane reforming, coal and biomass gasification, and plasma arc decomposition. Thermochemical cycles and biomass conversion, as well as hybrid thermochemical cycles also seem to be competitive to fossil fuel and biomass prices.

D. Energy Efficiency Comparison:

The efficiency data used in this study are taken from Holladay et al. [68], Ismail and Bahnemannc [69], Singh and Wahid [70], Ibrahim et al. [71], Bicakova and Straka [72], and

Dincer and Zamfirescu [73]. Table 2presents the energy and exergy efficiency data of selected hydrogen production methods from which it can be seen that fossil fuel reforming, plasma arc decomposition, and coal and biomass gasification are advantageous over other methods. On the other hand, photonic energy based hydrogen production methods show the poorest performance among the selected production methods.

Table 2: Comparison of various Hydrogen Production Methods.



Sr. No.	Method	Energy Efficiency	Exergy Efficiency	Cost	SCC	GWP	AP
1	Electrolysis	5.30	2.50	7.34	3.33	3.33	8.86
2	Plasma Arc Decomposition	7.00	3.20	9.18	0.83	0.83	5.14
3	Thermolysis	5.00	4.00	6.12	7.50	7.50	7.43
4	Thermochemical Water Splitting	4.20	3.00	8.06	9.17	9.17	9.43
5	Biomass conversion	5.60	4.50	8.10	6.67	6.67	2.00
6	Biomass Reforming	3.90	2.80	7.93	6.25	6.25	0.86
7	PV Electrolysis	1.24	0.70	4.50	7.50	7.50	7.71
8	Photocatalysis	0.20	0.10	5.19	9.58	9.58	9.71
9	Dark Fermentation	1.30	1.10	7.52	9.58	9.58	9.71
10	Fossil Fuel Reforming	8.30	4.60	9.28	2.50	2.50	5.71
11	Photoelectrolysis	0.78	0.34	7.09	8.33	8.33	9.71

IV. CONCLUSION

Thus after analyzing several methods, we can conclude that:

1. Fossil fuel reforming has the highest (83%) and photocatalysis (less than 2%) has the lowest energy efficiency. Biomass gasification has the highest exergy efficiency (60%), followed by fossil fuel reforming (around 45e50%). Again, photonic based hydrogen production options have lowest exergy efficiencies compared to other selected options.

2. According to production cost evaluation, fossil fuel reforming ($0.75/kg H2), coal gasification ($0.92/kg H2), and plasma arc decomposition ($0.85/kg H2) produce the cheapest hydrogen. Whereas, the newly developed method, photoelectrochemical hydrogen ($10.36/kg H2) is by far the most expensive one. GWP and AP of photonic based hydrogen production methods are close to zero. As a result, these options have very low SCC. Whereas, fossil fuel reforming, plasma arc decomposition, biomass and coal gasification possess very high GWP, AP, and SCC among the selected options.

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