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A Critical Review on Green Hydrogen

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Abstract

Hydrogen being one of the best alternative fuels to conventional fuels, it is expected to play a vital role in future Low-Carbon Economy. When hydrogen is produced using renewable sources, it is termed as green hydrogen. At present, Green Hydrogen is being produced via different technologies including, Thermo-Catalysis, Thermolysis-Electrolysis, Photo-Catalysis, Photo-prospects, Electrochemical process, and Bio-Photolysis etc. As Green Hydrogen production does not involve CO_2 emissions, it is going to be the potential candidate for deep de-Carbonization. Here, we will be reviewing different Green Hydrogen technologies and provide their comparison along with techno-economic assessment.

Keywords: Hydrogen, Alternative Fuel, CO_2emissions, Renewable energy, de-Carbonization

1. Introduction

Hydrogen has the potentials to become an important renewable source with some unique qualities. Due to abundant nature of hydrogen, theoretically production of hydrogen has no limits [1]. Hydrogen is light in weight, storable, and highly dense in heat value, where the heat value is defined as the amount of heat released during the combustion of a fuel, also termed as energy/heat value (Jkg^{-1}) [8]. Table 1 compares the heat value of H_2 along with the conventional and few organic fuels.

Table 1 Heat Values for H_2 gas and Different Fuels

Fuel	Heat Value (*MJ/kg*)
Hydrogen (H_2)	120-142
Methane (CH_4)	50-55
Methanol (CH_3OH)	22.7
Dimethyl ether - DME (CH_3OCH_3)	29 MJ/kg
Petrol/gasoline	44-46 MJ/kg
Diesel fuel	42-46 MJ/kg
Crude oil	42-47 MJ/kg
Liquefied petroleum gas (LPG)	46-51 MJ/kg
Natural gas	42-55 MJ/kg

Combustion of hydrogen does not emit any pollutants or greenhouse gases (GHG) [2]. The use of hydrogen as an energy source was identified in the 20th century, and from the past few decades a drastic improvement has been observed in the hydrogen market [4]. Hydrogen is going to play a prominent role in renewable energy economy and is expected to contribute to reduced GHG emissions, zero carbon economy and other societal benefits. Hydrogen is a great fuel for de-carbonization and de-fossilation of the world and it is going to help establish self-reliance in the energy sector [3],[4]. In the current scenario, hydrogen is primarily used in production of chemicals and fertilizers, petroleum industry, metal treatment, food processing industry and rocket fuel [6]. It can also be used for powering residential houses, industries, transportation and automobiles and it is expected to catch up in the automobile industry in the upcoming few decades [7]. Due to the increasing conventional fuel prices, and environmental concerns, huge investments are being made in the hydrogen infrastructure and economy [8]. The governments across the globe are focusing heavily on production of hydrogen with a strict need to focus on consumption of hydrogen in different sectors to cut down the GHG emissions. At present H_2 production from the renewable sources is costing two to seven times more than the H_2 produced from the natural gas without carbon capture [10]. Based on the reports of International Energy Agency (IEA), there was no significant progress in the area of Green Hydrogen until 2010 because of the limited capacity of H_2 production plants (<1 MW) through electrolysis. Recently this number has gone up with a greater number of hydrogen production plants with capacity up to 25 MW were installed. In March 2020, a 10 MW project was installed in Japan and another 20 MW plant was setup in Canada. Recently private sectors have invested for 700 MW electrolysers. As per IEA reports, a significant progress has been made in the recent past with promising opportunities for renewable sources with potentially lower costs, less energy loss and almost negligible GHG emissions [9]. However, there are a number of technical and commercial challenges for the green hydrogen economy including –(a) high costs of Green Hydrogen production, which is ranging between 5-7 US $ per kg, (b) limited demand for hydrogen in various industries, (c) non-availability of technologies for large scale green hydrogen production with storage and (d) lack of infrastructure for the same [6][7].

2. Types of Hydrogen

Based on the source of production, Hydrogen can be classified into three major categories as defined below -

***Grey Hydrogen**:* If hydrogen is produced from fossil fuels, then it is termed as Grey Hydrogen.

***Blue Hydrogen**:* If CO_2 is captured in the process of producing grey hydrogen using fossil fuels, then the resultant hydrogen is termed as Blue Hydrogen.

***Green Hydrogen**:* If the hydrogen is produced by electrolytic splitting of water, using renewable sources of energy with zero-carbon emissions than it is called Green Hydrogen.

In addition to the above, following sub-classification is also commonly known in the industries:

***Pink Hydrogen**:* If the hydrogen is produced through electrolysis of water using nuclear energy

***Turquoise Hydrogen**:* If hydrogen is produced via pyrolysis of Methane

***Yellow Hydrogen**:* If the hydrogen is produced via electrolysis of water using solar energy

***White Hydrogen**:* Naturally occurring geological hydrogen traced in underground deposits [14]

Technologies for production of Hydrogen

Hydrogen accounts for 0.14% by weight in the earth’s crust in total that too in the form of water. The logical sources of overall hydrogen present are hydrocarbons (from fossil fuel) and water present in the earth crust. At present 95% of hydrogen is being produced using fossil fuels as the main source including natural gas, oil and coal. The contribution of green hydrogen is only about 0.1% of the global hydrogen production. There are a number of different processes for production of hydrogen [11]. Thermochemical methods include production of hydrogen using fossil fuels, organic materials, and biomass. Splitting of water also results in the production of hydrogen, and there are different ways to do so including biological water splitting, solar water splitting, photoelectrochemical water splitting and renewable electrolysis. Bacteria and algae can be also used to produce hydrogen through various biological processes including photobiological and microbial biomass conversion [12].

Figure 1 Shows different processes used for production of hydrogen

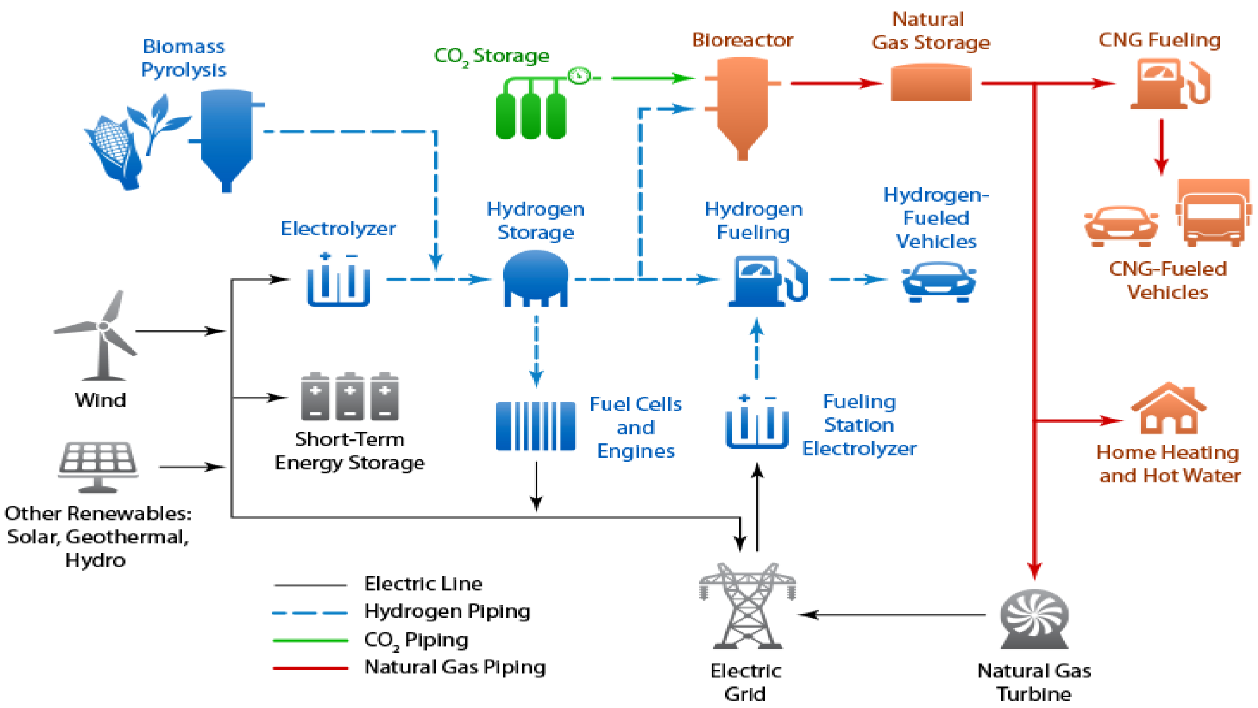

Figure 1. adapted from reference [13]

Production of Hydrogen following Thermo chemical Process

Natural gas reforming: At present, 95% of hydrogen is produced via reformation of natural gas which is also termed as steam methane reformation (SMR). In this process, hydrogen is produced from fossil fuels, such as methane or natural gas which are allowed to react with steam in presence of a catalyst, results in hydrogen and carbon dioxide. In case, when natural gas is used in SMR, it shows 72% efficiency [14][15], [16]. The reaction for SMR is shown below:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \text{Eq. (1)}$$

The process of SMR produces hydrogen rich gas with 70-75% of hydrogen on a dry mass ratio, in addition to 2-6% methane, 7-10% carbon monoxide and 6-14% carbon dioxide [17]. The cost of production from SMR is about $ 2-5 per kg on a large scale with delivery costs included [18] and this may vary based on the cost of the feedstock as well as the scale at which H_2 is being produced along with few other factors.

Gasification of Coal and other Hydrocarbons: Hydrogen can be produced using hydrocarbon fuels including heavy residual oil, coal and other low value refinery products in the process termed as Partial Oxidation (POX), also known as Gasification. The hydrocarbon fuel is allowed to react with oxygen in a less than stoichiometric ratio which results in production of carbon monoxide and hydrogen at temperature around 1200-1350 ^{0}C. The cost of production of H_2 from gasification process is about 2-2.5 US $ per kg [18]. Pyrolysis based hydrocarbon gasification in the absence of oxygen also results in the production of hydrogen at almost similar costs in the bulk quantity.

Hydrogen from Biomass: Biomass can be converted into valuable products including hydrogen with the help of methods including thermochemical and biochemical processes. The biomass feedstock is heated in the absence of oxygen resulting in production of a blend of hydrogen and carbon monoxide-rich stream of gas termed as ‘syngas’. A wide variety of biomass can be used as feedstock in the thermochemical process. In contrast, only wet, sugar-based feedstock can be used in biochemical processes to produce hydrogen. In addition to this, there is a great possibility to include cellulosic feedstocks in enzyme based biochemical processes, if it is possible to improve the process technique and systems. Fermentation and microbial assisted electrolysis are the biological feedstock-based processes, in which certain waste stream feedstock can produce hydrogen as a valuable product [15][19][20][21].

Table 3 Advantages and disadvantages of biomass derived hydrogen

Advantages	Disadvantages
Reduction in municipal solid waste	Limited and seasonal availability
Lowering CO_2 emissions	High cost
Improvement in agricultural output	Tars production
Replacement of conventional fossil fuels with sustainable biomass fuel	

The cost for thermochemical process is a bit low as compared to biochemical because it can be operated at high temperatures leading to higher reaction rates. The cost for hydrogen production is about $ 5-7 per kg if it is produced at medium scale industry, and it may further be reduced to as low as $ 1.50-3.50 per kg if it is possible to produce at larger scales. Hydrogen can be offered at low as $ 1.0 per kg, if produced via pyrolysis of biomass with large scale production and pipeline delivery systems in the long term. Depending upon the scale of production and specific requirements, an additional $ 1.0 per kg for purification and transportation can be added to the overall cost of hydrogen production [18].

When combined with carbon capture, utilization and storage (CCUS), biomass derived thermochemical and biochemical processes could potentially produce carbon negative hydrogen. To enable economic competitiveness of these techniques, there is need to focus on pre-treatment and transportation of feedstocks with improvement of conversion efficiency for the same [22]. Different technologies including gasification of coal, autothermal reforming and steam methane reformation can offer promising near-term option for net zero economy if combined with carbon capture and storage. Gasification and SMR are currently used in combination with CCUS at certain plants, yet there is a strict need to focus more on R&D in areas including process intensification, capital cost reduction, polygeneration, separation, catalysis, control and modularization so that the overall cost can be limited under less than $ 1 per kg of hydrogen produced.

Production of Hydrogen through Electrolysis of water: Water molecules can be directly split into oxygen and hydrogen molecules via a process known as **'electrolysis'** using electricity a device known as electrolysers [15].

The corresponding reaction can be written as

$$\text{Water} + \text{electricity} \rightarrow \text{oxygen} + \text{hydrogen}$$

Electrolysers can be classified on the basis of electrolyte used as alkaline if potassium hydroxide is used and PEM if a solid polymer membrane is used as electrolyte. The pure oxygen produced in the electrolysis as a by-product can be used for many useful processes including food processing. The electricity that needs to be supplied to carry out the process of electrolysis, can be generated from any electrical source including nuclear power, utility grid power, wind power, solar photo voltaic (PV) and hydropower.
Solar derived hydrogen would cost around $ 6-24 per kg which is expected to go as low as $3-8per kg whereas wind powered hydrogen is costing around $6-8 per kg of hydrogen produced.

Splitting of water using biological enzymes: Hydrogen can be produced from water as a part of metabolic process of certain photosynthetic microbes using light energy. Since splitting of water always produces oxygen as by-product along with hydrogen generation, there is a strict need to overcome the inherent oxygen sensitivity of hydrogen evolving enzymes. Research across the globe is being going on to address the issue by screening for oxygen tolerant naturally occurring enzymes that can produce hydrogen in the presence of oxygen [23][24].

Photoelectrochemical Water Splitting: Water can be directly split into oxygen and hydrogen using sunlight which results in the production of cleanest hydrogen. NREL has developed PEC system which produces hydrogen using sunlight without considering the use of electrolysers with a solar to hydrogen conversion efficiency of 12.4%. Photovoltaic industry has developed multijunction cell technology that can generate sufficient voltage to split the water [24].

Photoelectrochemical water splitting using CuO based electrodes for hydrogen production
The process of photoelectrochemical water splitting involves generation of clean hydrogen with no carbon footprints to facilitate the production of hydrogen. Solar energy is used to produce hydrogen at an electrode which is coated with special semiconductor or PEC materials [25].

Cupric oxide being one of the low-cost semiconductors shows high activity for photocatalysis of hydrogen evolution reaction (HER) in sunlight radiation, when combined with other photocatalysts.
Preparation of CuO particles: the suitable methods for preparation of CuO particles or thin films include Chemical vapor deposition (CVD)[26], spray pyrolysis, electrodeposition, sol gel, microwave irradiation synthesis, sono-chemical, template assisted, hydrothermal, thermal oxidation etc.

Disadvantages

- Poor performance of semiconductor materials
- Development of stable photoelectrodes with high resistance against photo-corrosion.
- Development of suitable semiconductors
- Development of inexpensive materials and electrodes

Solar Thermal Water Splitting

High flex solar furnace reactors have been in use by NREL researchers to generate temperature between 1000 to 2000 ^{0}C using solar concentrators for splitting of water to produce hydrogen. As reaction rate increase with increase in temperature, this technique offers a novel approach for the production of clean hydrogen [27].

Renewable Electrolysis

Renewable energy sources such as hydro, geothermal, wind, biomass, photovoltaics is considered as an enabler for decarbonization initiatives with fulfilling the needs of clean and sustainable electricity for the present and upcoming generations. However, we are well aware of the fact that renewable sources of energy are dependent on various factors including seasonal changes, geographical locations and availability. Thus, produced Hydrogen via renewable electrolysis can be used directly into fuel cell to produce electricity and stored for use at peak demand time. Researchers across the globe are examining various issues related to the renewable sources of energy for production of hydrogen via electrolysis to be used in fuel cells including design options, performance enhancement, and reduction in capital costs [28].

Production of Green Hydrogen by Recycling of Aluminum
According to Susana Silva Mortinez and Wendeylopez Benits [33] high purity hydrogen can be produced using aluminum cans waste with sodium hydroxide using caustic soda at very low cost. The displacement reaction corresponding to the generation green hydrogen is as follows

$$\text{Al + Acid or base} \rightarrow \text{Metal Compound + Hydrogen Gas}$$

The main reason for using Aluminum as anode is its high theoretical ampere hour capacity. In addition, Aluminium also shows high specific energy and voltage values. This method has several advantages which includes no carbon emission, high purity hydrogen as yield which can be directly used in PEM fuel cell to produce electricity and water. No external energy supply is required for this process and there is a good possibility of recycling of Aluminium and sodium hydroxide used in the above-mentioned process [29].

Cost of Green Hydrogen
As 1 kg of hydrogen has energy equivalent to 3 kg of natural gas, the overall cost of Green Hydrogen includes electricity costs, investment cost, and electrolysers cost which is about 2 to 3 times than blue hydrogen.

Challenges to future of Green Hydrogen
There are a number of technical and commercial challenges that include
Limited scope of hydrogen usage in various industries,
High cost of electrolysers
Non-availability of suitable technologies for large scale production of Green Hydrogen

- Lack of enabling infrastructure for Green Hydrogen production
- Limited demand for hydrogen is also a barrier.
- New electrolytes must be researched and developed to cut down the price.
- Lack of funding in green hydrogen sectors, although governments across the globe has started investing into the new possibilities in the area of green hydrogen but there is still a need of focusing on putting more investments into it.
- Not enough technologies

Future challenges:
In the future, following areas have to be focused to reach zero-carbon economy target with producing efficient, cost effective, sustainable and cleaner energy with the help of Green Hydrogen:

- Reformation technologies including Autothermal Reforming (ATR) should be available at cheaper capital costs.
- Low cost photochemical and thermochemical processes with high durability and novelty.
- Durable separation of materials and membranes at cheaper prices.
- Efficient, durable and high-performance low cost electrocatalysts and catalysts with reduced platinum group metals.
- Flexible and adjustable electrolysis and gasification system for distributed and bulk power systems
- Improved fuel cell systems [30]

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