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Research Paper

Green hydrogen production

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I. Introduction

Global climate change is the defining crisis of our time, and presently, the development of sustainable systems for clean energy is a top priority to tackle this situation. With the increase in human population, the global energy demand is increasing, with fossil fuels being the most consumed to power mechanized lifestyles, eventually contributing the most towards global greenhouse gas emissions (1, 2). The increased emissions and reliance on fossil-based energy sources have necessitated the need to switch to more environment-friendly types of fuels, for which hydrogen is considered a promising alternative to power a cleaner decarbonized future (3, 4). Hydrogen is a versatile energy carrier as it can help hard-to-decarbonize areas such as heavy industries and transportation, can substitute fossil fuels for chemicals and fuel production, and can store surplus renewable power mitigating the effects of global warming (5–9).

Depending on the energy source and the production methods used to make molecular hydrogen, it is commonly classified as grey, blue, and green hydrogen (10). Grey hydrogen is the most abundant form obtained by steam methane reforming of natural gas and coal gasification (11). Since these processes releases CO_2 into the atmosphere, grey hydrogen is not observed as a low-carbon fuel (12). Similar to grey hydrogen, a purportedly cleaner option is blue hydrogen, which is also produced from fossil fuels through steam methane reforming of natural gas or coal gasification, except that most of the CO_2 emissions are captured and kept underground utilizing carbon capture and storage (6, 11). Since the CO_2 emissions are reduced, blue hydrogen is considered a low-carbon cleaner alternative to grey hydrogen but is expensive due to the use of carbon capture and storage technology (6, 13). The majority of hydrogen derived through these processes is dependent on the combustion of fossil fuels, and the adverse environmental effects of these have diverted research interests towards the development of environmentally acceptable and contamination-free hydrogen. Green hydrogen, also referred to as 'clean hydrogen', is a form of hydrogen that can be produced during water electrolysis powered by energy from wind, solar, and biomass (3, 14). Since the process is fueled by renewable energy sources or biomass, the resulting hydrogen is pollutant free without any associated emissions of greenhouse gases (3, 14). The present article comprehensively describes methods for production of green hydrogen and their implementation for industrial and commercial applications, including transportation, shipping, and infrastructure.

Methods to produce green hydrogen

Green-hydrogen production technologies are presently not available with reasonable efficiency and cost. To accelerate the adoption of green hydrogen technologies globally under current conditions, different renewable energy-based hydrogen production methods are currently employed. Still, these methods require substantial research to increase production efficiency, yield and reduction in cost (6). Based on the raw material used to extract hydrogen, Miltner et al. classified several green hydrogen production techniques (15). These methods include electrolysis, thermolysis, hydrogen sulphide splitting, PV-electrolysis, photo-catalysis, bio-photolysis, enzymatic, photo-electrolysis, bio-photolysis, photo-fermentation, etc. (16–18). In another study, Tanksale et al. provided a summary of biomass-based catalytic hydrogen production and the biological processes of hydrogen generation were reviewed by Levin and Chahine (19, 20).

1. **Water electrolysis:** This is the most common method to obtain pure hydrogen after splitting water with the help of electricity, created by the flow of constantly circulating electrons through an external circuit. Despite technological advancements, only 4% of hydrogen can be produced globally via this method due to financial difficulties. (21–23). To overcome its limitations, the technologies for this method are continuously developed and upgraded. The technologies are divided into the following types based on operating conditions, ionic agents, and electrolytes: the proton exchange membrane water (PEM) electrolysis, alkaline water electrolysis, and the anion exchange membrane (AEM) water electrolysis, (24, 25). For industrial and commercial hydrogen generation of up to a multi-megawatt range, the alkaline water electrolysis is a well-known method that produces hydrogen at a relatively lower cost with long-term stability. (24). Here, the use of concentrated NaOH/KOH alkaline solution in the electrolyser allows it to function at lower temperatures. (24, 26, 27). Still, the main challenging part linked with this method is limited current densities, because of the moderate use of extremely concentrated alkaline electrolytes (25, 28). In addition, the purity of hydrogen and oxygen gasses generated is also low because the diaphragm cannot stop the diffusion of gasses from one half-cell to the other (25). AEM electrolysis is also a developing technology similar to traditional electrolysis, except that the traditional diaphragms are substituted with an anion exchange membrane, thereby enabling the operations at higher current densities (29). Some of its benefits include using low concentrated alkaline solutions and inexpensive catalysts in place of noble metal catalysts (29, 30). Nevertheless, the technology needs some advancements to increase its cell efficiency for scaling up its applications (31). When an acidic sulfonated polymer membrane is used as the electrolyte instead of a liquid electrolyte, the process is termed PEM electrolysis (25). Interestingly, PEM electrolysis produces higher current densities and highly pure gasses (hydrogen and oxygen) (25). This is faster and safer than alkaline electrolysis, but the high cost of cell components is its major drawback (25, 31).

2. **Biological routes:** An alternative way for the production of green hydrogen is from biological sources. Biohydrogen production is believed to be a cost-effective approach since the process can be performed in ambient conditions in an environmental-friendly manner with easy operational techniques. Several routes exist for the production of biohydrogen depending on the microorganism used and the substrate, such as photofermentation, indirect photolysis, microbial electrolysis, dark fermentation, and biophotolysis (24, 32–35). Direct photolysis is similar to the process of photosynthesis occurring in algae (*Chlamydomonas*, *Chlorococcum,* and *Chlorella*) and plant cells, where micro-organisms sensitive to light are used as bio-reactors to convert solar energy into hydrogen (33). Another similar process is indirect photolysis, wherein microalgae or cyanobacteria (*Oscillatoria*, *Calothrix, Anabaena*, and *Nostoc*) can produce hydrogen from starch or glycogen utilizing light energy (33). Dark fermentation is another carbon-neutral process carried out by anaerobic bacteria to produce hydrogen in a low oxygen environment from organic wastes (36). This process is accompanied by the production of toxic wastes, and the yield of hydrogen is also less. Photofermentive hydrogen production involves the conversion of organic substrates (butyrate, acetate, malate, succinate etc.) by photosynthetic microorganisms (*Rhodobacter sulfidophilus, Rhodobacter sphaeroides, Rhodospirillum rubrum,* etc.) (34, 35). A bio-device that interacts with photonic radiation was created and developed by Gust et al., that supplies electrons and photons to adenosine tri- phosphate (ATP) synthase enzyme, which produces ATP and eventually hydrogen from the substrate (37). Some hydrogenases found in algae or bacteria can also catalyse hydrogen production or oxidation depending on the catalytic potential of enzyme (38, 39). Some of the microorganisms used for biohydrogen production are listed in table 1.

Table 1: List of some microorganisms used for production of green hydrogen.

Microorganism	Substrate	Reference
Rhodopseudomonas palustris	Acetate, lactate, and malate	(40)
Escherichia coli	glucose	(41)
Enterobacter aerogenes	Xylose	(42)
Klebsiella oxytoca	Glucose	(43)
Clostridium acetobutylicum	Glucose	(44)
Clostridium beijerinckii	Raw food waste	(45)
Clostridium guangxiense	Peanut shells biomass	(46)

3. **Plasma arc decomposition:** The ionised state of matter known as plasma contains excited electrons and has the potential to be utilised as a conduit for the discharge of high- voltage electric current. (4, 47). The process involves the use of natural gas such as methane which separates to hydrogen and carbon black (soot) due to thermal plasma activity and requires high voltage (Table 2). The underlying principle relies on the

passage of methane through a plasma arc, which separates into carbon black (soot) and hydrogen as summarized by Fulcheri et al. (Table 2) (47).

4. **Water thermolysis**: A single-step process involving the splitting of water into hydrogen and oxygen by supplying thermal energy is termed thermolysis (Table 2). The process requires extremely high temperatures (above 2500 K) to have a fair level of dissociation (24, 48). Another drawback of this technique is to efficiently separate the generated hydrogen and oxygen, failing to which may lead to the production of an explosive mixture. To avoid this recombination of hydrogen and oxygen, the resultant gasses are quickly chilled by quenching through a sharp decrease in temperature within a few milliseconds (49–51).

5. **PV electrolysis:** Green hydrogen production via electrochemical water splitting is a promising approach for using solar energy as a clean fuel. This system couples an electrolyser with a photovoltaic (PV) power generation system that supplies electricity to electrolyser. The electrolytic water splitting eventually release water and oxygen. Mason and Zweibel analysed this system's effectiveness and cost (52) The technique is costly, and the yield of hydrogen is also relatively less, as analysed by Yilanci et al. (53, 54). Additionally, the solar energy when converted to chemical hydrogen energy via PV electrolysis has a conversion efficiency of close to 16%. For large-scale deployment of this method, the overall cost of solar based hydrogen generation should be significantly reduced. For this technology to be economically competitive, the development of a water splitting system with high solar-to-hydrogen (STH) efficiency is critically required (55).

6. **Wind electrolysis:** Wind energy is the cleanest and easiest process to produce green hydrogen. Producing hydrogen using direct wind electrolysis device requires a wind turbine generator, a water electrolyser, and a converter (AC/DC) that generates hydrogen and oxygen (56). Another configuration of this method involves a hybrid wind/grid-electrolysis that consists of a contribution of grid energy as an auxiliary energy to the wind turbine when there is no wind (56). Weather information such as wind speed, the direction of wind flow, temperature, humidity, pressure, rainfall, topographic data and roughness plays an essential role in improving this approach's productivity and efficacy (57). Despite a few drawbacks, several countries, such as the USA, China, India, etc., have adopted this method for bulk production of green hydrogen (57, 58).

Table 2: The chemical conversion reactions occurring in different green hydrogen production methods.

Green hydrogen production	Reaction
Electrolysis (4, 24)	$H_2O \xrightarrow{\text{Electrolysis}} H_{2\,(gas)} + 1/2\ O_{2\,(gas)}$
Dark fermentation (4, 59)	$\text{Biomass} \xrightarrow{\text{enzyme}} \text{organic acid} + H_2 + CO_2$
Bio-photolysis (59)	$H_2O \xrightarrow{\text{Light+bacteria/algae}} H_{2\,(gas)} + O_{2\,(gas)}$
Photo-fermentation (35, 59)	$\text{Biomass} + H_2O \xrightarrow{\text{Light+microorganism}} H_2 + CO_2$
Water thermolysis (49)	$H_2O \xrightarrow{\text{Heat}} H_{2\,(gas)} + 1/2\ O_{2\,(gas)}$
Plasma arc decomposition (4, 59)	$CH_4 \longrightarrow C_{(soot)} + H_{2\,(gas)}$

II. Conclusion

Hydrogen is now emerging as a clean energy source and green hydrogen offers a decarbonization solution to the industrial, chemical, power generation and transportation sectors. Despite the unique possibilities and advantages, the complete replacement of fossil fuels and fossil fuel-based feedstock with green hydrogen or its derivatives has so far been hindered by supply issues, unfavourable cost economics, lack of unified standards and regulations, and expensive enabling infrastructure. With a few upgradation strategies and technological advancements, green hydrogen represents a promising source for cleaner energy in shaping the future.

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