

REVIEW ARTICLE

HYDROGEN VIA BIOLOGICAL AND PHOTO-CATALYTIC TECHNOLOGIES

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ABSTRACT

Hydrogen, a clean and renewable energy source, is currently being researched and developed as a promising alternative to decarbonize the energy sector. It offers carbon-free fuel flexibility and energy storage for the global grid. There are various technologies for hydrogen production, including biological and photo-catalytic methods. This review paper discusses these technologies, their aspects, challenges and potential advancements. The reviewed work indicates that current biological hydrogen technologies generally have lower yields and conversion efficiencies and are only applicable to a minority of biomass materials. However, they are sustainable, environmentally friendly and operate at low temperatures. Similarly, photo-catalytic hydrogen technology is also environmentally friendly and sustainable, using natural sunlight and water to generate hydrogen with minimal greenhouse gas emissions. Nevertheless, its efficiency is still lower than other methods such as steam methane reforming and electrochemical electrolysis of water.

KEYWORDS

Substrate, fermentation, photo-fermentation, photo-catalytic, water gas shift reaction.

1. INTRODUCTION

A 2021 report by the International Energy Agency has highlighted the alarming levels of global energy and CO₂ emissions, which have become a major concern due to the unprecedented levels of greenhouse gas emissions. The main cause of this worrying trend is the burning of fossil fuels for energy production, leading to the release of harmful gases such as CO₂, CO, SO₂, NO_x and ozone, as well as pollutants like lead, soot and ash (IEA, 2021). Complicating the situation further is the depletion of fossil fuels and the projected 50% increase in global energy demand by 2040, driven by population growth and industrialization in developing regions like Asia and South America, as highlighted in a 2014 IEA report (IEA, 2014). Consequently, addressing an impending energy crisis and preventing environmental pollution has become an urgent priority. Therefore, there is an urgent need to find a clean, renewable, cost-effective and sustainable energy source as an alternative to fossil fuels.

Hydrogen has become a focal point as a renewable and eco-friendly energy carrier. Its ability to decarbonize the energy sector by offering carbon-free fuel flexibility and energy storage for the global grid has attracted significant attention (Zainal, et al., 2024). Various methods and processes are employed to produce hydrogen gas from different sources, collectively known as hydrogen production technologies. These technologies encompass biological production, photo-catalytic production, thermochemical production and electrochemical production. Biological production involves the use of microorganisms or their enzymes to generate hydrogen from various organic substrates through biological processes (Pal, et al., 2022). Generally, biological processes for hydrogen production are considered more environmentally friendly and sustainable compared to electrochemical and thermochemical processes (Zhang, et al., 2024). Photo-catalytic production involves the use of semiconductor photo-catalyst(s) (Ishaq, et al., 2021) to split water or other substrates into hydrogen, as a clean energy carrier (Hassan, et al., 2023), and oxygen

under the influence of sunlight (Luo, et al., 2021). Photo-catalytic processes are also environmentally benign and sustainable, although some greenhouse gas emissions are also generated (Hassan, et al., 2023; Zhang, et al., 2024). Electrochemical production, on the other hand, uses electricity to drive chemical reactions that result in hydrogen production (Dotan, et al., 2019). Water electrolysis is commonly employed in electrochemical hydrogen production technologies (Anwar, et al., 2021). Electrochemical processes mainly rely on electrolysis technologies such as alkaline electrolysis, anion exchange membrane, proton exchange membrane, solid oxide electrolysis and bipolar membrane electrolysis. This method is considered environmentally friendly and sustainable for large-scale hydrogen production (Zhang, et al., 2024). Thermochemical production involves high-temperature chemical reactions to produce hydrogen from various feedstocks (Guban, et al., 2019). Among the main thermochemical processes for producing hydrogen are steam methane reforming, partial oxidation, auto-thermal reforming, dry reforming and gasification of coal and biomass. Generally, thermochemical methods are broadly used for large-scale hydrogen production, through steam methane reforming; in particular (Zhang, et al., 2024).

This paper specifically examines the biological and photo-catalytic technologies used for hydrogen production, delving into their distinct characteristics, obstacles and potential advancements.

2. TECHNOLOGIES OF HYDROGEN PRODUCTION

2.1 Hydrogen Via Biological Technology

Biological processes for hydrogen production involve the use of enzymes or living microorganisms to convert organic substrates into hydrogen through metabolic processes (Pal, et al., 2022). These methods are often considered more environmentally-friendly and sustainable compared to thermochemical and electrochemical processes (Zhang, et al., 2024). By utilizing waste materials or sunlight, biological hydrogen production

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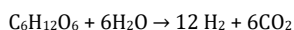
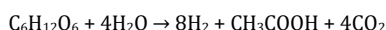
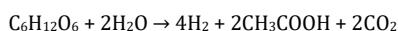
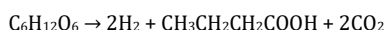
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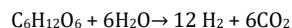
results in lower levels of greenhouse gas emissions and typically operates at low temperatures, reducing energy requirements for hydrogen generation (Zhou, et al., 2020). The benefits of biological processes in hydrogen production are numerous. By converting organic waste into hydrogen, these methods can contribute to the renewable energy mix (Gautam, et al., 2023). Hydrogen produced through biological processes has various applications in agriculture, such as generating power and producing bio-fertilizers and biofuels (Huber, et al., 2006; Singh, et al., 2018; Sharma, et al., 2020). Approximately 50% of hydrogen use in agriculture is for the production of ammonia-based fertilizers (Ball and Weeda, 2015). Currently, biological processes for hydrogen production include dark fermentation and photo-fermentation.

Dark fermentation, or more accurately, dark heterotrophic fermentation (light-free), is a process used for hydrogen production. Various organic materials such as wastewater, organic waste, lignocellulosic biomass and carbohydrates can be used as organic substrates (Łukajtis, et al., 2018; Zhang, et al., 2019; Arun, et al., 2022). The selected substrate should contain a high amount of fermentable elements, such as sugars and organic acids. In some cases, pretreatment may be necessary to convert complex organic compounds into simpler molecules that are easier to ferment (Kucharska, et al., 2020). Pretreatment techniques can involve enzymatic, physical or chemical processes, depending on the substrate selected for the fermentation process (Zhang, et al., 2024). Out of this fermentation process, hydrogen can be produced by introducing an anaerobic microbial culture, composed of mixed bacteria at temperatures between 25 and 80 °C or higher as required according to the strains used, into a bioreactor with the substrate (Kapdan and Kargi, 2006; Argun, et al., 2009). The organic compounds are then broken down by the microorganisms in an anaerobic environment to be compatible with that of the microbial culture (Rasheed, et al., 2021). This involves a number of complicated biochemical events; the targeted microalgae or bacteria produces gaseous hydrogen in multiple phases of hydrolysis. The first phase involves the enzymatic hydrolysis of organics with high molecular weight into water-soluble organics. In the second phase of hydrolysis, simpler organics are hydrolyzed into volatile fatty acids, CO₂ and gaseous hydrogen along with some biomass and residues of fermentation products (Kapdan and Kargi, 2006; Argun, et al., 2009). In order to purify the produced gaseous hydrogen from CO₂ gas and other liquid byproducts, gas sparging and membrane separation or adsorption techniques should be used; respectively, ready for compression/liquefaction for storage/liquid transportation, as desired. Whereas biomass and remaining fermentation products are either disposed of or processed further for energy recovery or nutrient recycling, depending on the process design and environmental regulations (Rasheed, et al., 2021). The reactions that describe hydrogen generation through dark fermentation are as following (Argun, et al., 2009):

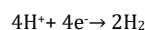
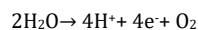


Also in this regard, another biological process for hydrogen production is photo-fermentation. Opposite to dark fermentation process, photo-fermentation does not work if there is no sun light or an artificial source of light (Zagrodnik and Laniecki, 2015; Sagir, et al., 2017; Zhang, et al., 2024). It depends on the metabolic conversion of organic molecules to bio-hydrogen through photosynthetic of several bacterial species (Zagrodnik and Laniecki, 2015; Sagir, et al., 2017). For a photo-fermentation process, those volatile fatty acids produced from a dark fermentation process as byproducts or from other anaerobic process(es) can be utilized as organic substrates (Mishra, et al., 2019). Out of this photo-fermentation process, hydrogen can be produced by inoculating photo-synthetic bacteria, e.g., purple non-sulfur bacteria, into an illuminated bioreactor containing the substrate (Chen, et al., 2023; Zhang et al., 2024). Either natural or artificial light sources must be used to illuminate the bioreactor in order to provide the necessary energy for hydrogen photo-synthesis. Out of this, with the aid of anaerobic and light conditions, gaseous hydrogen is produced, in addition to, some CO₂ with some other gases and liquids. In order to purify the produced gaseous hydrogen from CO₂ gas and other liquid byproducts, similar techniques to those used in dark fermentation should be used, rendering hydrogen ready for compression/liquefaction for storage/liquid transportation, as desired (Zhang, et al., 2024). Photo-fermentation can be completed in one or two steps. Although the photo-fermentation with one step is cheaper than two steps photo-fermentation, it; however, suffers from high energy consumption, as well as limited solar energy conversion. In the two steps photo-fermentation, in an effort to generate more hydrogen, photo-fermentation is carried out after a dark

fermentation. The two steps photo-fermentation process is disadvantageous due to complicated operation due to different bacteria and operational parameters involved among the different phases (Zagrodnik and Laniecki, 2015; Sagir, et al., 2017). Thus, both photo-fermentation processes are less commercially competitive than other biological processes for hydrogen generation (Azwar, et al., 2014). The chemical reaction of applying photo-fermentation on glucose, as a model substrate, is shown in following equation (Hallenbeck and Liu, 2016):



Recent research and development have focused on exploring cutting-edge biological technologies for the production of hydrogen. By utilizing these advanced biological methods to generate hydrogen from organic materials, there is potential to significantly improve the efficiency, environmental sustainability, and cost-effectiveness of hydrogen production through this approach (Zhang, et al., 2024). For instance, microorganisms, e.g., microalgae/cyanobacteria, due to their capability to produce hydrogen via oxygenic photosynthesis and nitrogenase enzyme activity can be converted into bio-hydrogen (also referred to as blue-green algae) through a direct/an-indirect biophotolysis process that uses the sun light or a controlled light to influence the microbial system by which water is disassociated into hydrogen and oxygen at a ratio of 2:1 with no CO₂ or any intermediary metabolic-producing events compared to dark fermentation (Kosourov, et al., 2017; Lam, et al., 2019; Veeravalli, et al., 2019; Kamshybayeva et al., 2023). The cyanobacterial strain is grown in a photobioreactor or open pond system with carefully regulated light, temperature, and nutrient levels to enhance growth and hydrogen production (Sadvakasova, et al., 2020). By inducing nitrogen depletion or other stressors, the activity of the nitrogenase enzyme is stimulated, resulting in the production of hydrogen within the cyanobacteria (Zhang, et al., 2024). Furthermore, the biophotolysis of water by organisms such as cyanobacteria and green microalgae could produce a clean and sustainable energy and based on a renewable source. Also, among the advantageous of this process is that it only uses the sunlight and CO₂ as a source of energy to generate hydrogen by the hydrogenase enzyme process via bacteria and algae (Ghirardi, et al., 2000). Moreover, biophotolysis processes require no substrate as nutrients where water is the main donor of electrons to generate hydrogen. The direct biophotolysis process illustrated in Figure (1) advances according to the following two reactions (Show, et al., 2018).



Another enhanced biological technology for hydrogen production is the bio-electrochemical systems which also use organic materials including biomass or wastewater as substrates (Sharma, et al., 2023). Electro-active microorganisms are introduced into a bioreactor fitted with an anode and a cathode, separated by an ion exchange membrane. These electro-active microorganisms could oxidize organic substrates at the anode, producing electrons and protons. The electrons travel through an external circuit, while the protons penetrate through the ion exchange membrane to the cathode, where they are converted into gaseous hydrogen (Al-Mamun, et al., 2023). Furthermore, another advanced biological technology for hydrogen production is the microbial consortia which are utilized to increase hydrogen production by using organic materials, e.g., wastewater, organic waste, lignocellulosic biomass and carbohydrates as substrates (Tomasini, et al., 2023). These consortia are added to a bioreactor with the substrate, where they break down the organic compounds and generate hydrogen gas, as well as some other by-products (Joshi, et al., 2023). Both engineered and naturally occurring microbial consortia, consisting of various types of bacteria and other microorganisms, are designed to improve rates of hydrogen production, yields and substrate utilization (Ergal, et al., 2022).

Furthermore, hydrogen can be generated via a bio-catalyzed electrolysis process. In this process, various dissolved organic compounds can be efficiently converted into wastewater via electrochemically active microorganisms that can generate an electrical current (biological anode) once the organic compound is oxidized. Connecting this anode to a cathode through a power supply results in reducing the protons, generating hydrogen. There are two basic types of bio-catalysis electrolysis-based bio-electrochemical systems which are microbial fuel cells and microbial electrolysis cells. The first system uses cathodes open to air, produces electricity and reduces air (Logan, et al., 2006). However, in the second system, an external power input is required to improve hydrogen generation at the cathode (Rozenal, et al., 2006). Green hydrogen can also be generated out of a bio-electrochemical system that uses microorganisms as catalysts to electrochemical reactions from various

substrates at the cathode and anode, to which heterotrophic bacteria is attached (Logan, et al., 2008; Lee et al., 2010; McCormick et al., 2013). This bacteria oxidizes the organic matter, found; for instance, in wastewater treatment facilities and food processing plants, to generate protons and electrons at the anode. Then, electrons are transferred to the cathode, while protons are reduced into hydrogen. To this end, this system

generates a green hydrogen and also could reduce waste streams. Bio-catalytically electrolysis of acetate using the second system, where only 0.14 v is required (Zainal, et al., 2024), is shown by the following chemical reaction equation (Zöhrer, et al., 2014).

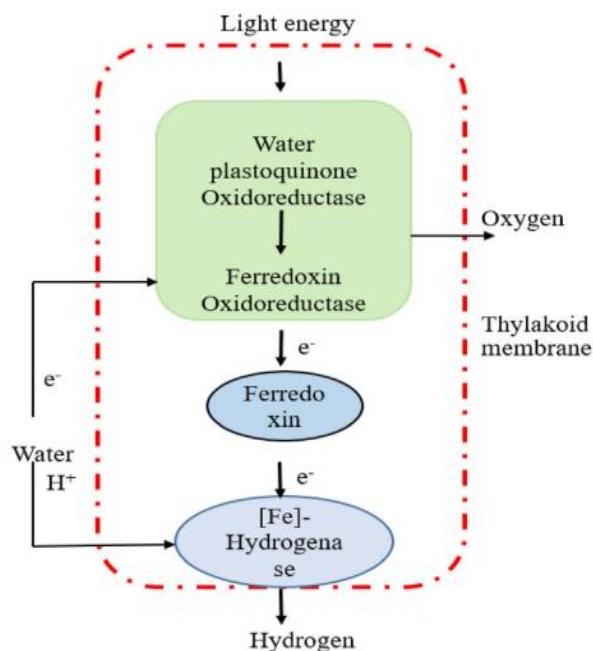
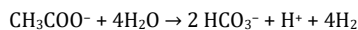
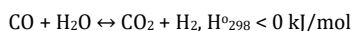


Figure 1: A Flow Diagram of Hydrogen Production via Biophotolysis (Show, et al., 2018).

In addition to the above discussed biological processes, biological water gas shift reactions can also be a route for hydrogen production. Although, unless the heterotrophic-bacteria, of carboxydophilic hydrogenogens of the Rhodospirillaceae family, *Rhodospirillum rubrum* or *Carboxydotherrmus hydrogenoformans*, is capable to use CO as a carbon source, a biological water gas shift reaction might not take place (Hosseini et al., 2015; Alfano and Cavazza, 2018; Veeravalli et al., 2019). The biological water gas shift reaction relies on the capability of these microbes in the dark to generate hydrogen accompanied by CO₂ through oxidizing CO and reducing water as indicated in the following equation of chemical reaction (Tanksale, et al., 2010). Biological water gas shift reactions are better than thermochemical water gas shift reactions as the former requires lower temperatures of no higher than 30-70 °C depending on the strain used and the surrounding pressure. However, excessive production of CO resulting from the feedstock, which results in reducing the bacterial activity, the need to the improvement of microorganisms, in order to improve their concentration in the bioreactor, and issues arising during gas to liquid mass transfer are all challenges should be addressed prior to the commercialization of the process of biological water gas shift reactions (Alfano and Cavazza, 2018).



Nevertheless, despite their sustainability and environmentally-friendly nature, biological hydrogen technologies currently have lower hydrogen yields and conversion efficiencies compared to thermochemical and electrochemical processes. This is mainly due to inherent limitations of the biological systems used (Lepage, et al., 2021). Additionally, these technologies can only handle a limited range of biomass materials such as sludge, agricultural and household wastes (Cohen, et al., 2022). Furthermore, the scaling up and optimization of biological hydrogen production technologies remain challenging, as they are relatively new and lack advancements in genetic engineering and synthetic biology (Ferraren-De et al., 2021; Zhang et al., 2024).

2.2 Hydrogen Via Photo-Catalytic Technology

In addition to biological methods of hydrogen production discussed earlier, hydrogen can also be produced through photo-catalytic technology. This process involves using water or other substances, such as waste biomass and renewable organic waste, under the influence of light to produce hydrogen using semiconductor photo-catalysts (Ishaq et al., 2021; Selvi and Sagadevan, 2022; Shi et al., 2023). The most commonly used photo-catalytic technology for hydrogen generation is the direct splitting of water into hydrogen and oxygen, which will be further discussed in this review. The light source can be natural sunlight or

artificial light, which initiates the photo-catalytic reaction by exciting the photo-catalyst (Fan and Tahir, 2022). The choice of photo-catalyst is crucial as it significantly impacts the effectiveness of the photo-catalytic process (Qutub, et al., 2022).

Among the commonly used photo-catalysts for hydrogen production via water splitting include a variety of metal oxides semiconductors such as CdS (Qutub, et al., 2022), TiO₂ nanoparticles (Qutub, et al., 2022; Selvi and Sagadevan, 2022), SnO₂, Fe₂O₃, ZnO, CeO₂, ZrO₂, WO₃, V₂O₅ (Selvi and Sagadevan, 2022) and V₂O₅ nanorods (Jayaraj et al., 2018), etc., to name a few. Among these, TiO₂ nanoparticles has been reported as the most promising one due to its complex structure, high surface area, high activity and content of noble metals (Chiarello and Selli, 2010). A photo-catalyst with a is a material that converts light energy into chemical energy by absorbing photons. Remarkable stability, a suitable band-gap energy, low level of toxicity (Suligoj, et al., 2022), advantageous electronic structure, biocompatibility, capacity to produce charge carriers when exposed to sufficient light energy, charge transport properties and excited lifetimes of these aforementioned metal oxides have rendered them suitable for use as photo-catalysts (Selvi and Sagadevan, 2022). Furthermore, the material of a photo-catalyst, is synthesized and, depending on the application, can be tailored to a suitable geometry, e.g., nanoparticles, thin films or immobilized on a support material. Also, in order to enhance, reaction kinetics, light absorption and charge separation by a photo-catalyst, its surface chemistry can be altered (Suligoj, et al., 2022).

A standard semiconductor photo-catalytic process for hydrogen production is schematically shown in Figure (2). A photo-catalytic process advances by placing the selected photo-catalyst in an open pond or a closed system photo-reactor, e.g., micro-photo-reactors or LED-based packed bed photo-reactors, etc., in reference to application and available process design. In both scenarios, the photo-reactor should promote light absorption and mass transfer while prevent back-reactions of hydrogen and oxygen (Zhang, et al., 2024). Then, water is added to the photo-reactor and the system is illuminated with a source light, which as mentioned earlier, can be either the natural sunlight or an artificial light. The light works to initiate the photo-catalytic reaction as it excites the photo-catalyst to create pairs of electron-holes. Once these electrons are produced, they are used to convert (reduce) water into gaseous hydrogen at the photo-catalyst surface, while the holes created in the process are responsible for oxidizing water to produce oxygen (Fan, and Tahir, 2022). The hydrogen and oxygen gases that are produced are then separated from each other and from the liquid phase. The hydrogen that is collected is subsequently purified, compressed or liquefied in order to be stored or transported, as required (Zhang, et al., 2024).

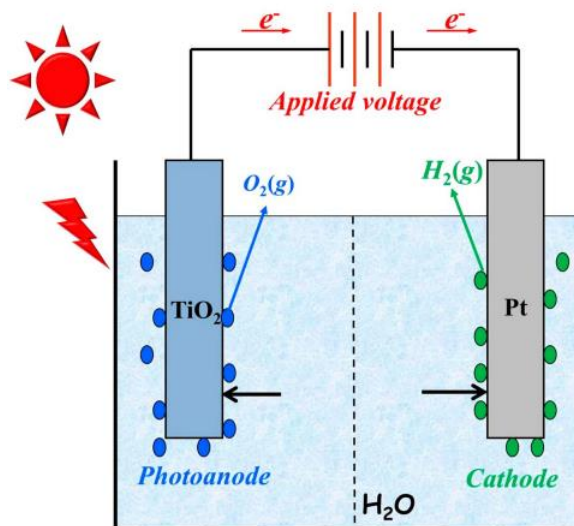


Figure 2: A Standard Semiconductor Photo-catalytic Process for Hydrogen Production (Li et al., 2016).

Li et al., found that photo-catalysts in various systems exhibit comparable processes for photo-catalytic hydrogen production. These processes typically involve light absorption, separation of charges, migration and transportation of charges, utilization of charges, self-corrosion caused by charges and surface back reaction (Li, et al., 2016). Specific removal rate of pollutants, apparent reaction rate constant, space time yield, electrical energy consumption and photo-catalytic space time yield are all important factors for a viable photo-catalytic process. Optimization of a photo-catalytic process includes considering parameters such as hydrogen peroxide, pH, temperature, UV light intensity, photo-catalyst load, dissolved oxygen, dissolved oxygen, air flow rate, type and concentration of pollutant, flow rate, ozonation and irradiation time. In this regard, attention should also be paid for the band-gap energy of photo-catalyst, pollutant absorption wavelength and wavelength of light source. In terms of the design of photo-reactors, although generally micro-photo-reactors may have the highest efficiency, LED-based packed bed photo-reactors show better performance when throughput is taken into consideration, thanks to their numerous interconnected micro-channel pockets. Furthermore, the design of a highly efficient photo-catalyst, in terms of its bulk and surface properties, as well as its electronic structure, requires a comprehensive consideration and optimization of thermodynamics and kinetics of light harvesting, charge separation, charge migration charge transport and charge utilization, self-corrosion by charges and surface back reaction. This is essential for a higher overall efficiency of a photo-catalytic process for hydrogen production (Li, et al., 2016). Furthermore, in order to achieve an optimal design for a photo-catalytic reactor, it is essential to balance two key parameters including technical feasibility and economic viability. Technical feasibility encompasses factors such as high throughput and performance, specifically in terms of mass transfer. On the other hand, economic viability involves considerations such as energy efficiency, particularly in relation to photon transfer, as well as overall cost (Sundar and Kanmani, 2020).

While water splitting through photo-catalysis for hydrogen production has shown promise as a sustainable technology, recent advancements in photo-catalytic technologies have focused on developing improved photo-catalysts using novel materials, nanostructures and hybrid systems to further enhance the overall efficiency and performance. Research is currently underway to enhance light absorption, charge separation and reaction kinetics through the use of narrow band-gap semiconductors, doped materials and ternary or quaternary compounds (Zhang et al., 2023). Additionally, various nanostructured photo-catalysts such as nanowires, nanorods and quantum dots have been synthesized to improve light absorption, charge transport and overall photo-catalytic efficiency (Guo, et al., 2022). Hybrid photo-catalysts, which combine different materials such as organic-inorganic or semiconductor-metals, have also been developed to enhance efficiency and stability in photo-catalysis (Zhou, et al., 2022). These hybrid systems take advantage of synergistic effects between materials, leading to enhanced charge separation and reduced recombination. Furthermore, tandem or Z-scheme photo-catalytic systems have also been developed by pairing two or more different photo-catalysts with compatible band-gap alignments to utilize a broader range of the solar spectrum and minimize charge recombination, ultimately enhancing the overall efficiency of solar-to-hydrogen conversion (Ayodhya, 2023; Zhang et al., 2024).

In summary, the process of producing hydrogen through photo-catalysis

is an eco-friendly and sustainable method that uses sunlight and water to produce hydrogen while minimizing greenhouse gas emissions. This technique is crucial in the renewable energy sector as it harnesses solar energy to produce clean hydrogen (Hassan, et al., 2023). The generated hydrogen can be utilized for storing solar energy for future use, supporting grid stability and managing energy efficiently (Zhang, et al., 2024). Nevertheless, the efficiency of photo-catalytic hydrogen production is lower compared to other methods such as steam methane reforming of thermochemical technology or electrochemical electrolysis of water (Oh, et al., 2022). Also, some photo-catalytic materials are susceptible to photo-corrosion or deactivation, leading to reduced effectiveness and the need for frequent replacement or regeneration (Vikrant, et al., 2019). Furthermore, the reliance on sunlight for photo-catalytic hydrogen production limits continuous generation due to the intermittent nature of sunlight (Rahman, et al., 2022). Moreover, there is a need for significant advancements in the design of photo-reactors, light capture systems and overall performance of photo-catalytic processes to enhance their efficiency (Zhang, et al., 2024).

3. CONCLUSIONS

Some of the technologies for hydrogen production that have been examined include biological and photo-catalytic methods. Biological technologies include dark fermentation and photo-fermentation with bio-electrochemical processes, bio-catalyzed electrolysis and biological water gas shift reactions. Biological water gas shift reactions are preferred over thermochemical water gas shift reactions due to their lower temperature requirements, typically ranging from 30-70 °C depending on the strain used and surrounding pressure. However, biological hydrogen technologies generally have lower yields and conversion efficiencies compared to thermochemical and electrochemical processes, mainly due to inherent limitations of the biological systems used. Scaling-up, optimization and advancements in genetic engineering and synthetic biology are needed to address these challenges. Similarly, photo-catalytic technology for hydrogen production also faces issues with lower yields and conversion efficiencies compared to methods like steam methane reforming thermochemical technology and electrochemical electrolysis. Additionally, the reliance on sunlight for photo-catalytic hydrogen production adds complexity to the process. Significant improvements in photo-reactor designs, light capture systems and overall performance are necessary to enhance efficiency. Despite these challenges, nevertheless, both biological and photo-catalytic technologies, are environmentally-friendly and sustainable, with minimal greenhouse gas emissions.

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