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An Updated Review on Biomass-based Hydrogen Production

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Abstract: One of the most significant renewable energy sources in the coming decades will be hydrogen. Recently, most of the hydrogen in the world has been produced using fossil fuels and their derivatives. Hydrogen can also be produced from readily available biomass. The biomass-based methods have several advantages, such as eco-friendliness, carbon neutrality, and renewable energy sources. Before the commercialization of hydrogen as a fuel, some technological, economic, and environmental challenges must be overcome. This article provides an updated review of the concept of green or biohydrogen, the importance of hydrogen in different fields, and biomass-based production methods. A total of 127 articles have been reviewed and cited in this manuscript.

Keywords: green or biohydrogen; renewable energy carrier; biomass-based methods.

1. Introduction

High energy demand results from the world's growing population and economy. Fossil fuels have fulfilled the need for energy, but due to their rapid depletion, these traditional sources are in a precarious position [1]. Energy and associated activities are becoming increasingly necessary to support human well-being, advancement in society and the economy, and healthcare. To fulfill the energy requirements of future generations, resorting to renewable energy sources is a great strategy to mitigate climate change [2]. Global environmental problems and rising greenhouse gas emissions necessitate an upgrade from conventional to renewable energy sources [3]. The hydrogen economy is an idealistic term for the integrated system of hydrogen generation, storage, and social use [4].

Large amounts of hydrogen are used in the chemical, petroleum, automobile, pharmaceutical, and alternative fuel industries, which suggests that its production will continue to increase. Hydrogen has the highest combustion energy discharge per mass among commonly used fuel sources [5,6]. Around 96% of hydrogen has been estimated to be produced from conventional fossil fuels, with 48% from steam reforming of natural gas, 30% from naphtha reforming, and 18% from coal gasification. Still, evidence suggests an interaction between global environmental contamination and conventional hydrogen production methods [7]. Several methods, such as thermal, electrolytic, and photolytic, can produce hydrogen [8]. Recently, there has been much interest in the prospective utilization of renewable biomass as a key feedstock for hydrogen production. The production of hydrogen from biomass has to be improved as soon as possible [9]. Biomass, used for manufacturing a range of biofuels, is one of the most promising renewable resources. Due to increased economic activity, biomass energy would benefit local society and contribute to a consistent energy supply [10]. Biochemical and thermochemical conversions of biomass to hydrogen are the two basic methods. Typically, the thermochemical process is more rapid than the biological process and provides more hydrogen [11]. A desirable and feasible alternative to conventional hydrogen production methods is biological production. The synthesis of hydrogen using biological methods has two significant obstacles: a low hydrogen yield and a high cost of manufacture [5]. The biological production of hydrogen is based on bio-photolysis, fermentation, and hybrid reactor systems. Thermochemical conversion techniques, such as pyrolysis, steam gasification, steam reforming of bio-oils, and supercritical water gasification, can convert environmentally favorable feedstocks into hydrogen [9].

2. Hydrogen, green hydrogen, and hydrogen production methods

Hydrogen has an atomic number of one, and the molecular formula is H_2. Hydrogen is a nonmetal placed on the left side of the periodic table with the first group of alkali metals [12]. Hydrogen is an odorless and colorless gas and the cleanest fuel. Hydrogen is non-polluting and has the potential to be an excellent energy carrier. To tackle the world's energy concerns, some significant obstacles must be overcome before hydrogen can be widely used in a sustainable future energy infrastructure [13]. Hydrogen is used in petroleum refining, food processing, transportation, the production of chemicals, energy storage, etc. Producing hydrogen via partial oxidation, splitting, photolysis, steam methane reforming, coal gasification, electrolysis, and other processes is feasible. The fuel sources and different processes used for producing hydrogen molecules, such as green, blue, grey, and other forms, are therefore used to categorize the different types of hydrogen [14-18] (Table 1). Hydrogen is more suitable for spark ignition (SI) engines than compression ignition (CI) engines due to its unique characteristics. Several studies involving hydrogen use in SI engines have been conducted to solve problems like low volumetric efficiency and lower power density [19]. Table 2 compares the fuel characteristics of hydrogen, natural gas, diesel, and gasoline [19-23].

Table 1. Types of hydrogen based on sources/processes.

Type of hydrogen	Sources/processes	References
Blue	Fossil fuels and CO_2 are captured and stored underground	[15]
Black/brown	Coal gasification	[16]
Green	Water splitting via renewable electricity or renewable biomass	[14]
Grey	Fossil fuels via steam methane reforming	[16]
Pink	Electrolysis of water via nuclear energy	[17]
Yellow	Electrolysis of water using solar energy	[18]
Turquoise	Pyrolysis of methane	[18]
Purple	Splitting of water via chemo-thermal electrolysis	[16]
Red	High-temperature catalytic splitting of water using nuclear power thermal	[17]
White	Naturally occurring hydrogen	[16]

Table 2. Comparison between the fuel properties of diesel, gasoline, natural gas, and hydrogen.

Fuel properties	Hydrogen	Natural gas	Diesel	Petrol
Density (kg/m^3)	0.089	0.754	830	730-780
Auto ignition temperature (K)	858	553	523	623
Lower heating value (MJ/kg)	119.7	50.2	42.5	44.8
Volumetric energy constant (MJ/m^3)	10.7	34 to 58	33 x 10^3	35 x 10^3
Combustion speed (m/s)	2.993	0.355	0.867	0.356
Latent heat of vaporisation (kJ/kg)	446	509	-	348
Minimum ignition energy in air (mJ)	0.02	0.29	0.24	0.24

Fuel properties	Hydrogen	Natural gas	Diesel	Petrol
CO_2 emission	0	9.5	13.4	2.52
Octane number	0	120	30	86 to 94

However, hydrogen produced from renewable resources has no emissions and is regarded as a green fuel. The use of green hydrogen is a substitute for traditional energy sources. So long as the process is carried out with energy from renewable sources, there are no greenhouse gas emissions [7]. However, the primary way of producing hydrogen nowadays is by converting fossil fuels, which constitute 96% of production. This is hardly a method that will make sustainable energy possible. However, there's a greener way to produce hydrogen [4]. The main obstacles to developing and growing a hydrogen economy are the shortage of green hydrogen-producing facilities and hydrogen transportation and storage infrastructure [24-26]. Recent energy roadmaps and national strategies aimed at carbon neutrality by 2050 show that green hydrogen is one of the prominent accelerators of the energy transition and the decarbonization of our societies [27]. Molecular hydrogen may be produced from biomass, water, and fossil fuels. Such sources must always possess abundant energy needed to obtain hydrogen from them [11,28]. Fossil fuel processes transform products obtained from fossil fuels that contain hydrogen. These methods are gasification, pyrolysis, and reforming. A key challenge in establishing a hydrogen-based economy is the removal of sulfur, which is present in most fossil fuels [8]. Renewable resources comprise water and biomass, where hydrogen is also produced. Hydrogen has been produced from biomass via biological and thermochemical processes. Thermolysis, electrolysis, photo-electrolysis, and bio-photolysis are used to produce hydrogen from water [11,13,28]. Figure 1 depicts the overall standard methods for hydrogen production [29-35].

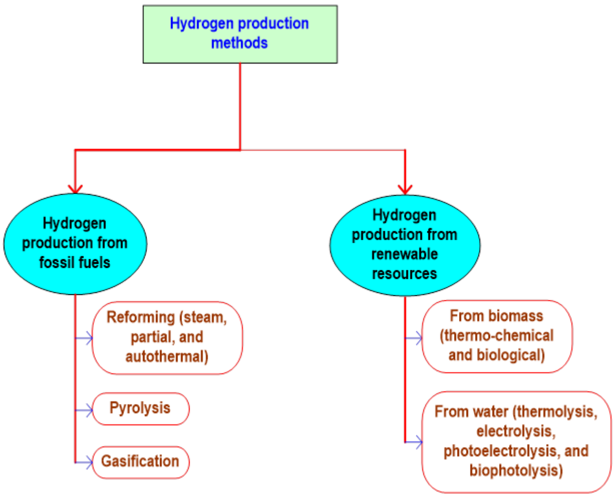

Figure 1. Standard hydrogen production methods.

3. Biomass-based production methods

Hydrogen is considered a potential energy source because of the restricted fossil fuel supplies, rising fuel costs, and growing pollution driven by worldwide energy demand. Hydrogen can be derived from renewable resources such as water and biomass. Renewable energy is now known as superior cleansing energy [36]. Hydrogen derived from biomass might be considered a significant energy source. Biomass has a lower carbon impact and is renewable compared to fossil fuels. Producing hydrogen from biomass has some challenges. Biomass produces a small amount of hydrogen since it has a low energy and baseline hydrogen content [37]. Due to an increase in the economy, energy from biomass would be advantageous to the local society and provide a steady energy supply. Biomass can be produced using waste biomass, growing certain energy crops, and harvesting plant and tree remnants [38].

3.1. Thermochemical methods.

Biomass thermochemical conversion yields a variety of liquid, solid, and gaseous fuels and is likewise relevant from an industrial and ecological aspect [39]. Thermochemical production of hydrogen using various biomass types is considered a viable and economically appealing method. Hydrogen may be produced from various kinds of wet biomass via thermochemical processes, eliminating the chemical addition requirement. There is still more to be done to progress most thermochemical conversion processes, and there are several obstacles, such as variable equipment prices, feedstock supply, practical obstacles, and public opinion [40]. Thermochemical methods include pyrolysis, gasification, and supercritical liquid [41] (Fig. 2).

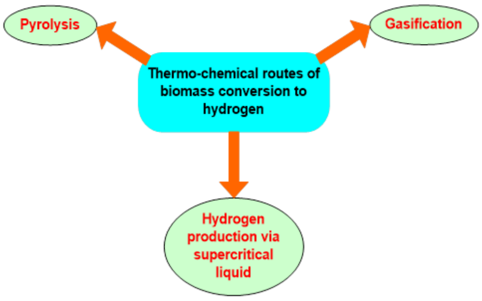

Figure 2. Thermochemical methods for hydrogen production.

3.1.1. Pyrolysis.

A thermal decomposition process of biomass called pyrolysis is carried out in an inert environment. This process of transforming biomass into products with additional value has been used frequently [42]. Typically, pyrolysis is carried out using a variety of process modes, such as slow and rapid decompositions of biomass material carried out at a high temperature in an inert atmosphere [43]. Through this process, the long-chain hydrocarbons of biomass breakdown down into smaller molecules in order to produce gas products, biochar, and bio-oil. Non-condensable gases like CO, H_2, carbon dioxide (CO_2), and methane (CH_4) are produced during pyrolysis. The highest reaction temperature and heating rate distinguish fast and slow pyrolysis [44]. The selected biomass is pyrolyzed and then transformed into gas, bio-oil, and char. Hydrogen is produced from bio-oil via steam reforming (Fig. 3).

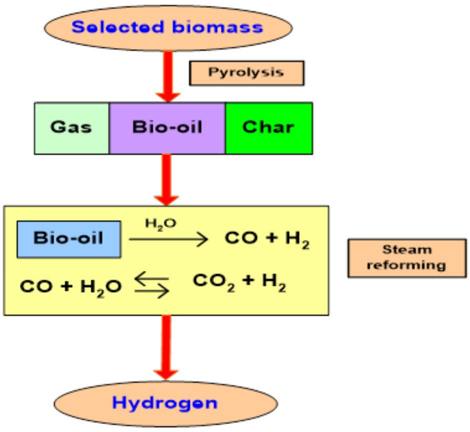

Figure 3. Hydrogen production via biomass pyrolysis.

The process of producing hydrogen (and carbon dioxide) from hydrogen carriers in the presence of water is known as steam reforming [45]. Synthesis gas, or hydrogen-rich gas, is produced by steam reforming. A high purity of hydrogen is produced through additional unit operations on the synthesis gas [46,47]. The most commonly used technique to produce hydrogen at a high rate is steam reforming of methane (SRM). The primary advantages of SRM include its relatively low temperatures, which are cost-effective, and the production of syngas that are high in hydrogen. SRM usually takes place at temperatures higher than 500 °C [45]. The SRM of methane is completed as below:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$

Steam reforming has the benefit of producing the highest possible output of hydrogen. The major endothermic reaction's considerable heat load and continuous supply of heat are the reaction's two main obstacles [48]. Exothermic processes take place during partial oxidation. The process commonly proceeds faster than steam reforming and requires a smaller reactor vessel. This method initially yields less hydrogen per unit of input fuel than steam reforming. The partial oxidation process provides high methane conversion with excellent hydrogen selectivity at relatively high space velocities. Due to challenges such as a slight reduction in CO selectivity brought on by overoxidation, partial oxidation has not yet been commercialized [49]. Using reactors that are considerably smaller and simpler than with present-day technology, catalytic partial oxidation methods can produce very nonequilibrium products without carbon production [50].

Wang *et al*. [51] studied the pyrolysis of cellulose for hydrogen production and then followed plasma-assisted reformation. The studies have been conducted with different reaction parameters such as steam, catalyst, discharge power, and reforming temperature. Wang and co-workers [52] reported that the incorporation of sodium and in-situ carbon dioxide (CO_2) capture in dental waste-derived sodium zirconate (DW-SZ) substantially enhanced hydrogen production in biomass pyrolysis. In order to produce hydrogen during the pyrolysis of three different biomass samples (municipal sludge, spirulina, and methylcellulose), the functional material that was produced later on was used. In the presence of functional material, spirulina provided the highest hydrogen yield compared to others. The pyrolysis of biomass derived from coconut wood was investigated by Suprianto *et al*. [53] to produce hydrogen. The biomass was pyrolyzed at 550°C, and the addition of curcumin and activated carbon to the biomass significantly increased the production of hydrogen (25.6%). The pyrolysis/gasification of wood sawdust biomass containing plastic with and without a Ni/Al_2O_3 catalyst has been investigated by Alvarez *et al*. [54]. As a result of adding 20 wt (weight) % of polypropylene to the biomass, the gas yield increased to 56.9 wt %, and the hydrogen concentration and generation increased to 36.1% and 10.9 mmol H_2, respectively. Arregi *et al*. [32] reported a fluidized bed reactor for producing H_2 using Ni catalyst and pine wood sawdust at 500 °C. This was followed by in-line steam reforming of the pyrolysis vapors. At the largest space-time investigated (30 gcat min gvolatiles^{-1}), for a steam/biomass ratio of 4, and at a maximum H_2 production of 117 g per kg of biomass, outcomes were accomplished.

3.1.2. Gasification.

Gasification of biomass is a typical thermochemical process based on the partial combustion of raw biomass. The higher organic hydrocarbons can break down into lower-molecular-weight combustible gases like CO, H_2, and CH_4 [55]. Processing a gaseous fuel must be done to produce heat and power for small- to large-scale applications. This opens up a more comprehensive range of technological possibilities. Compared to the direct combustion of solid fuels, producing energy from gaseous fuels is probably more efficient. Refining biomass feedstocks into gaseous fuels has the potential to contribute to a cleaner conversion [56]. Figure 4 depicts the basic process involved in gasifying biomass into hydrogen. Most chemical processes that produce hydrogen involve the water-gas shift (WGS) reaction [57]. The WGS reaction is required because the gaseous output of a gasifier commonly consists of significant volumes of hydrogen and carbon monoxide, along with smaller amounts of other gases [58]. This reaction is presented below:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

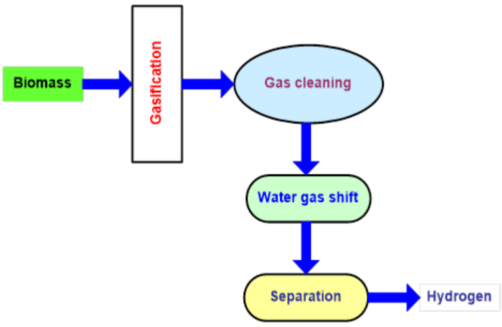

Figure 4. Hydrogen production via biomass gasification.

Jin *et al*. [59] studied the catalytic gasification of biomass in a fixed-bed reactor using Ni-based catalysts with Ca addition. The hydrogen yield increased from 10.4 to 18.2 mmol/g sample in the presence of a Ca-based catalyst. The amount of hydrogen produced following the amount of nickel present inside the catalyst increased from 50 g of nickel per mole (with a catalyst containing 0.1 mol% of Ca) to 80 g of nickel per mole (with a catalyst containing 0.8 mol% of Ca). The sorption-enhanced gasification of biomass with steam in a fixed-bed reactor has been reported by Zhang *et al*. [60]. The present study has clarified the effects of temperature, catalyst type, and loading on hydrogen production. When K_2CO_3 was utilized with a 20 wt% K loading, the most significant carbon conversion efficiency (88.0%) was attained at 700 ^{0}C, corresponding to a hydrogen output of 73.0 vol %. Li *et al*. [61] reported a novel two-step staged biomass gasification for hydrogen production. The ability of biomass to be gasified at a higher temperature in the first stage and then reformed at a lower temperature in the second stage was enhanced by the independent handling of each stage. In the presence of sorbent CaO and the effects of different operation conditions, biomass steam gasification was reported by Acharya *et al*. [62]. At steam/biomass ratios of 0.83, CaO/biomass ratios of 2, and a temperature of 670 °C, product gas with hydrogen concentrations as high as 54.43% is produced.

3.1.3. Hydrogen production via supercritical liquid.

Supercritical water gasification (SCWG) is a potential alternative energy conversion method. The ability of SCWG to produce hydrogen from biomass has recently sparked a lot of interest. In the drying process, SCWG advances without consuming much energy and improves process efficiency [63]. Aqueous organic wastes or wet biomass can be completely gasified using the SCWG technique under appropriate reaction conditions to yield hydrogen-rich gas [64] (Fig. 5). Supercritical water (SCW) is a suitable candidate for the gasification process due to its distinct and adjustable physico-chemical properties. SCW behaves in the properties of gases above critical pressures and temperatures without any phase change. Water becomes a non-polar solvent when the number of hydrogen bonds across the critical point and the dielectric constant significantly decrease [65]. Gasification of biomass is facilitated by SCW in an excellent reaction environment [66].

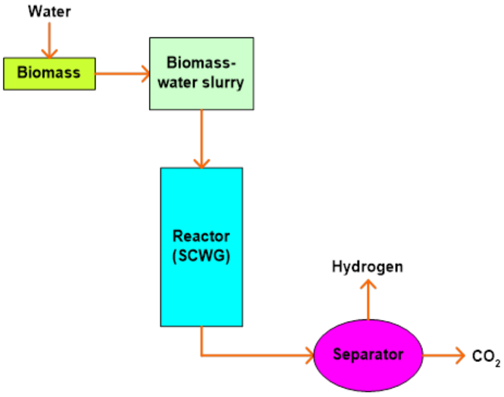

Figure 5. SCWG for biomass conversion to hydrogen.

Reddy *et al*. [67] reported that the SCWG effectively produces hydrogen because it prevents biomass drying and enables optimum conversion. Process conditions must be higher than 374 °C and 22.1 MPa for biomass to be converted to gases. In SCWG, the reaction temperature, feed concentration, residence time, pressure, and catalysts play a crucial role. The SCWG is a sophisticated and successful method for converting biomass to hydrogen, as stated by Zhao *et al*. [68]. Four machine-learning models were reported in this study. The maximum energy efficiency (43.3%) and hydrogen reaction efficiency (45.6%) were found when biomass with a high O-content and low H/C ratio was used as feedstock. Lu *et al*. [69] have reported the SCWG to be a promising method for the efficient utilization of wet biomass for the production of hydrogen. The present study demonstrated the impact of pressure, solution concentration, residence time, and temperature. Compared to other factors, temperature was shown to be the most important for hydrogen production. The SCWG of biocrude for hydrogen production was reported by Tushar *et al*. [70] under different conditions. It has been demonstrated that temperature has no effect on the biocrude's carbon gasification efficiency. The equilibrium conditions for the biocrude under consideration have been attained at a lower temperature in terms of carbon conversion. Ibtissem *et al*. [71] conducted SCWG of glycerol in mini-autoclaves to carry out a study on optimizing hydrogen production. Results showed that for efficient hydrogen synthesis and gasification, a high temperature and a long residence time are preferred. In addition, the pressure change has no discernible impact, while the rise in the initial glycerol concentration has a detrimental impact.

Further, the main advantages and disadvantages of the above-mentioned thermochemical methods are shown in Table 3.

Table 3. Main advantages and disadvantages of thermochemical methods.

Methods	Advantages	Disadvantages
Pyrolysis	Simple and fast process and formation of biochar, bio-oil, and gas products.	Catalysts deactivation, sensitivity of feedstocks.
Gasification	High yield of hydrogen, reliability, and efficient process.	Formation of ash, tar, and other residues.
Supercritical liquid	Non-corrosive processes and wet biomass can be directly gasified.	A low heating rate can reduce the efficiency of the process and increase the formation of tar.

3.2. Biological methods.

Biomass is now a significant renewable energy source that can substitute fossil fuels in order to sustain a green community and expedite the growth of the circular bioeconomy [72]. The conversion of biomass is one of the emerging techniques for producing hydrogen, as it is low-cost, clean, and renewable. In practice, biological processes can be used to produce hydrogen [73]. Environmentally benign and less energy-intensive, biological hydrogen production can operate at ambient pressure and temperature [74-77]. It is very challenging to develop bioreactors, regulate the reaction conditions, and estimate hydrogen production capacity due to the fact that the biological hydrogen production reaction process is so complex and necessitates dealing with multiple unsteady and nonlinear interactions [78]. Furthermore, because any organic waste may be used in these processes, they may be able to tackle issues with waste disposal and energy generation [79]. Figure 6 depicts the classification of biological methods for hydrogen production [80-82].

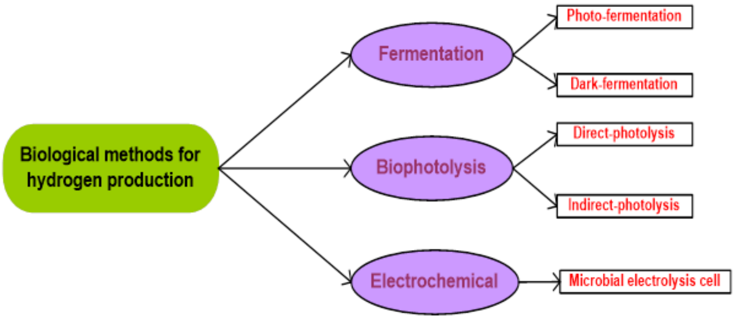

Figure 6. Biological methods for hydrogen production

3.2.1. Fermentation.

Hydrogen is produced easily and rapidly via fermentation. This technology can utilize a range of organic wastes as substrates for the fermentation process to produce hydrogen. This process allows for treating organic waste and generating extremely clean energy [83]. The composition of the organic substances required to produce hydrogen significantly affects its performance. Carbohydrates, including glucose, xylose, and sucrose, are the ideal substrates for hydrogen production owing to their high degradation rate. Proteins can only produce a small amount of hydrogen when they are broken down into amino acids. Lipids, which contain glycerol, are likewise inappropriate for the production of hydrogen [84]. The two different types of fermentation for hydrogen production are photo-fermentation and dark fermentation [81].

3.2.1.1. Photo-fermentation.

A photo-fermentation is an organic substrate fermentative reaction involving photosynthetic bacteria and light energy. It is an anoxic reaction where organic molecules such as lactate, acetate, and butyrate are broken down and produce H_2 and CO_2 when exposed to light [85]. Electrons and protons formed during the oxidation of organic substances are used in the photo-fermentative hydrogen production process [86]. Due to the pleasant conditions for reactions, the utilization of solar energy, and efficiency, the photo-fermentation process is a very promising approach [87]. In anaerobic conditions, PNS (purple non-sulfur) photosynthetic bacteria can produce hydrogen from organic acids; this process extends the potential for producing hydrogen from various materials, such as organic acid-rich waste and effluent [88].

The mechanistic pathway of photo-fermentation is presented in Figure 7. The fermentation process depends significantly on PNS bacteria. Light-harvesting complexes and different reaction centers are present in these bacteria. Light energy is absorbed by light-harvesting complexes in order to obtain electrons from carbon sources. Electrons are first transported to nitrogenase through an electron transfer chain and ferredoxins.

Light can dramatically increase the synthesis of nitrogenase, which is essential for hydrogen generation [89]. Barghash *et al*. [90] studied a single photo-fermentation technique using landfill leachate as the substrate for hydrogen production. This process was based on pH values and temperature. As a result, the pH values that were taken into account were 6, 6.5, and 7.2, respectively, at a regulated temperature of 37°C. A medium pH scale of 6.0, a fermentation temperature of 37 ±1°C, and a constant shaking speed of 100 rpm led to maximum hydrogen production.

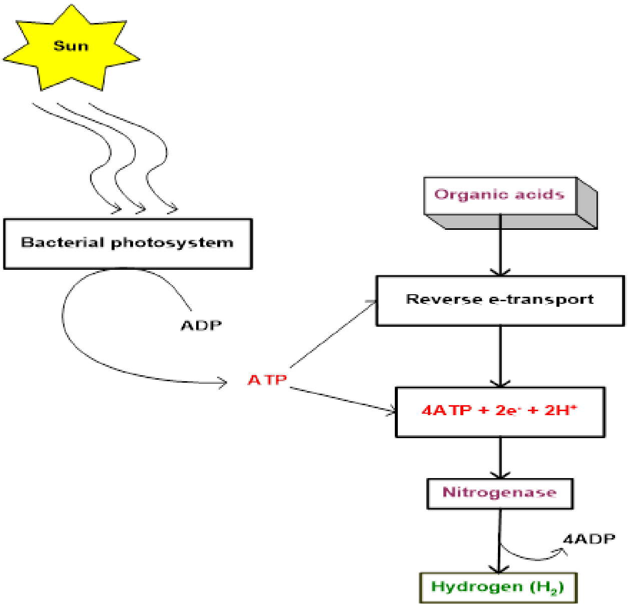

Figure 7. Mechanism of photo-fermentation.

Lu *et al*. [91] investigated the effects of Fe^{2+} and Fe^{3+} in the fermentation broth using corn stalks for hydrogen production via photo-fermentation. With an energy conversion efficiency of 5.21%, which was 19.98% greater than no-addition, the maximum hydrogen generation of 70.25 mL/g was found at 2500 μmol/L Fe^{2+} addition. The effect of the initial pH of the buffer on the photo-fermentation process of producing hydrogen was examined by Guo *et al*. [92]. The findings showed that the initial pH values of the phosphate buffer had a substantial impact on the photofermentation process. At an initial pH of 6.5, the greatest rate of hydrogen synthesis was 23.96 mL/h. The maximal production of hydrogen rates declined with the initial pH values at 5.0 and 7.5. Cai *et al*. [93] reported that integrating dark- and photo-fermentation is a viable approach to enhance the effectiveness of saline wastewater treatment and hydrogen production. The control was a dark fermented broth that had not been pretreated. The hydrogen output (134%) and substrate utilization (67%) were enhanced with the addition of photo-fermentative bacteria after dark fermentation. Bosman *et al*. [94] studied microbial photo-fermentation's potential to yield hydrogen. The operation of a thermosiphon photobioreactor and the impact of diurnal light cycles on *Rhodopseudomonas palustris* growth and hydrogen productivity were both investigated with an automated system. In the thermosiphon photobioreactor, diurnal light cycles that approximate daylight hours were found to lower hydrogen synthesis, exhibiting a lower maximal production rate than continuous illumination.

3.2.1.2. Dark fermentation.

Dark fermentation is conducted by anaerobes (facultative and obligate) in the absence of oxygen and light. These bacteria act on the substrate during the fermentation and produce hydrogen [95]. The conditions of the bioreactor must be optimized for efficient bacterial growth, as the metabolism of bacteria yields carbon dioxide and hydrogen as byproducts. The mixture of gases is collected and can be used as a renewable energy vector [96]. Various renewable organic wastes have been explored as potential substrates for dark fermentative biohydrogen generation, including rice straw, vegetable waste, food waste, sugarcane molasses, oil palm sap, cassava, wheat straw, etc [97].

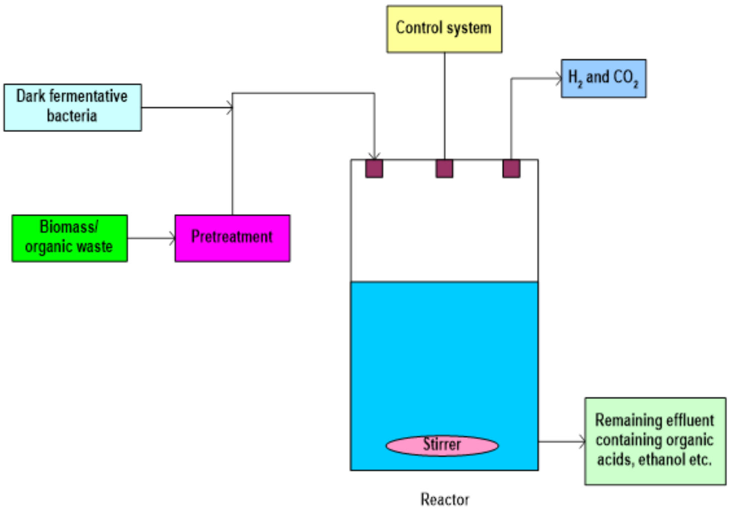

Figure 8. An outline diagram for dark fermentation.

Some of the main advantages of dark fermentations include an efficient hydrogen production rate as compared to photo-fermentation, no requirement for light energy, low cost, and easy design of bioreactors [98]. Dark fermentation has become more widespread than other biological methods to produce hydrogen due to its efficiency and independence from light [99]. Figure 8 depicts an outline diagram for dark fermentation. Figure 9 presents an outline of the bio-hydrogen production route via dark fermentation [100-102]. The basic fermentation reaction in dark fermentation is given below:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 2H_2 \qquad (4)$$

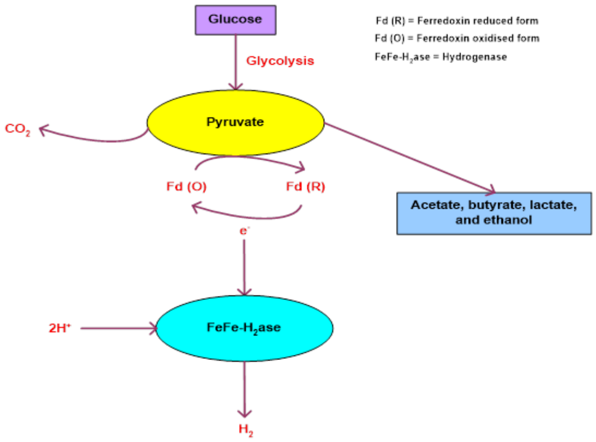

Figure 9. An outline of the bio-hydrogen production route via dark fermentation.

Hovorukha *et al*. [103] investigated the production of hydrogen via dark fermentation as well as the decomposition of solid and liquid waste from fruits, vegetables, meat residue, alcohol, and sewage. In terms of solid waste, hydrogen yields were 102 L/kg and liquid waste, 2.3 L/L. The weight of the solid waste decreased by 91-fold due to the fermentation process, and the amount of organics in the liquid waste was reduced by 3 fold. Potassium ferrate (PF), a strong oxidant, was used in the anaerobic dark fermentation of food waste by Kuang *et al*. [104] to produce hydrogen. Experiments showed that PF enhanced food waste-to-hydrogen generation. Through the use of synthetic wastewater in the fermentation process, the rapid PF oxidation prevented the processes of hydrolysis, acetogenesis, acidification, methanogenesis, and homoacetogenesis. A sequential dark fermentation and microbial electrochemical cell (MEC) process using food waste was reported by Jia *et al*. [105] for producing hydrogen. The results demonstrate that anaerobic digested sludge produces biogas at rates and hydrogen proportions that are higher than those of anaerobic granular sludge. Ghimire *et al*. [106] reported the dark fermentation of olive mill wastewater, rice straw, and food waste to produce hydrogen. The maximum hydrogen yields were observed at an initial pH of 4.5 and 5.0. The yield of hydrogen was found to be doubled using olive mill wastewater as compared to rice straw and food waste. Eker and Sarp [107] conducted a dark fermentation using waste paper, which led to hydrogen production. In order to examine the impact of sugar concentration on the production of hydrogen, various concentrations of glucose, which were extracted from waste paper, were used. At an initial sugar content of 18.9 g/L, the maximum cumulative hydrogen gas was produced.

3.2.2. Biophotolysis.

Biophotolysis is also known as water-splitting photosynthesis. In this process, oxygenic photosynthetic microorganisms such as green algae and cyanobacteria produce hydrogen in the presence of water and sunlight. The applicability of green microalgae requires hydrogenase and heterocystous cyanobacterial nitrogenase is used in this process [108]. Water has been broken down by these bacteria into hydrogen and oxygen via direct or indirect biophotolysis. Green algal hydrogenase promotes the evolution of hydrogen in direct biophotolysis. Nitrogenase in blue-green algae accelerates nitrogen fixation during indirect biophotolysis. The electron transport chain, which is made up of PS-I (photosystem-I) and PS-II (photosystem-II), serves as the place where electrons that arrive from splitting water pass. The action of ferredoxin-generating adenosine triphosphate (ATP) results from its reduction. These influence several chemical processes that lead to the synthesis of hydrogen [109]. In direct photolysis, water is split into oxygen and hydrogen; cyanobacteria and microalgae have this capability. Algae have developed to such an extent that they can now use solar energy to obtain protons and electrons from water. Water splitting takes place as sunlight is absorbed and electrons move to hydrogenases and nitrogenases [110]. Pigments at PS-I and PS-II, or both, absorb light energy, increasing the energy level of water oxidation electrons when transported from PS-II via PS-I to ferredoxin. Hydrogen gas directly retains some of the light's energy [111]. The transport of electrons is facilitated via PS-I and ferredoxin (Fd). By using the plastoquinol generated via electron transfer to reduce $NADP^+$ (Nicotinamide adenine dinucleotide phosphate) to nicotinamide NADPH (Nicotinamide adenine dinucleotide phosphate hydrogen). Photosystem II uses these water-derived electrons for photosynthesis. For the production of ATP through ATP synthase, a proton gradient is necessary. These protons serve as the electrons' terminal acceptors [81]. Figure 10 depicts the process of direct photolysis. In direct biophotolysis, the main drawbacks include oxygen sensitivity and a poor light conversion rate. Implementing an oxygen-inactivation-resistant hydrogenase along with oxygen absorbers is a way to address this problem [112].

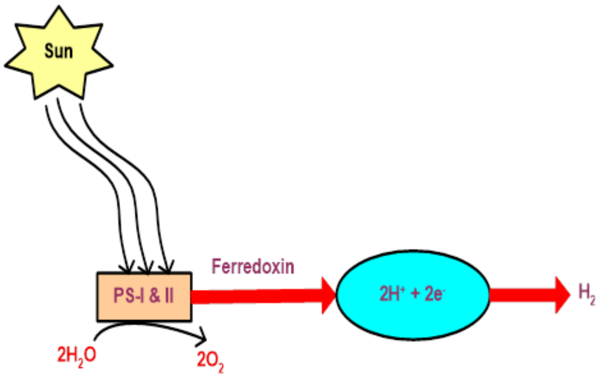

Figure 10. Direct photolysis.

The formation of hydrogen and oxygen takes place in distinct reactions in the two stages of indirect photolysis (Fig. 11). Glycogen and starch, both found in cyanobacteria and microalgae, function as intracellular reserves in the formation of hydrogen [113]. Cyanobacteria and green algae, which mainly produce hydrogen using electrons obtained from the catabolism of carbohydrates, are used in the process [87]. Water molecules split into protons and oxygen in the presence of sunlight during the first step. Carbon dioxide is fixed, synthesizing storage carbohydrates, and then hydrogenase produces hydrogen gas in the second step. The fact that hydrogen evolution is separate from oxygen evolution is advantageous. The considerable ATP consumption of nitrogenase and the constant light supply are some of the drawbacks [38].

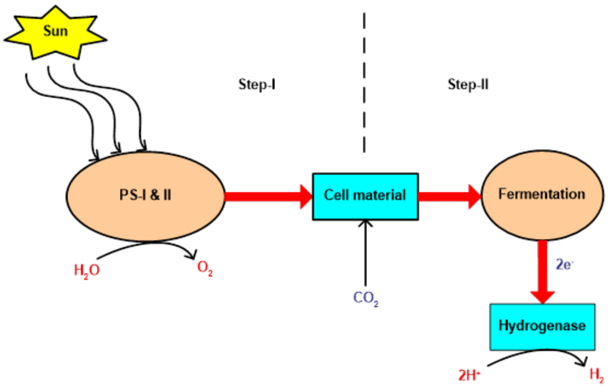

Figure 11. Indirect photolysis.

Direct photolysis using *Chlamydomonas reinhardtii* to produce hydrogen has been reported by Ban *et al*. [114]. Algal cells could retain high amounts of protein and chlorophyll by adding Ca^{2+} ions. For the protection of the PS-II activity, which is in charge of direct photolysis H_2 generation, high chlorophyll and low ROS (reactive oxygen species) were favorable. This study investigates rapid and simple methods for increasing the production of H_2 from algal photolysis. Ban *et al*. [115] reported that *Pseudomonas* sp. strain D has been shown to be an essential partner that helps *Chlamydomonas reinhardtii* promote photolysis-mediated H_2 generation. It is also an excellent partner for fostering H_2 production by the green algae *Chlorella* and *Scenedesmus*. Algal-bacterial collaboration increased starch content, maintained protein levels, and slowed the loss of chlorophyll. These are the prospective elements whose control offers a chance to increase algal H_2 generation. Zarei and others [116] reported a sustainable and environmentally friendly technique for hydrogen production via a photobioreactor. An affordable and sustainable method of producing hydrogen has been identified, which involves the growth of cyanobacteria in an internal-loop airlift photobioreactor. Hupp *et al*. [117] reported that eukaryotic green algae (*Chlorella*) have the potential for the production of hydrogen. It has been observed that the bacterial partners *Bacillus amyloliquefaciens*, *Bacillus mycoides*, and *Bacillus cereus* substantially improve algal biomass yield. The production of algal hydrogen was clearly related to effective bacterial respiration.

3.2.3. Electrochemical.

A microbial electrolysis cell (MEC) is a biochemical approach used to produce hydrogen via oxidation and reduction reactions [118]. MEC is an innovative renewable energy technology that simultaneously eliminates pollutants such as heavy metal ions, dyes, and others from industrial, municipal, and agricultural wastewater. MEC is still in its initial stage due to the cost of membranes, design, electrodes, etc., and it encounters difficulties in large-scale applications [119]. Waste-to-product conversion occurs in the presence of electrochemically active bacteria without harming the environment [120]. Carbon-based anodic materials are generally used in MEC because of their chemical stability, availability, and conductivity. Such materials also prevent stable bacterial interactions due to their hydrophobic nature. It has been suggested that hydrophobicity patterns can be eliminated via acid and heating treatments. One of the additional methods to enhance bacterial adherence is immobilization using organic polymers [121]. The main parts of MEC are the anode, cathode, and separator (Fig. 12). Protons and electrons pass through the electrolyte and the external electric circuit and come together to form hydrogen at the cathode. A microbial biofilm on the electrode serves as an electrocatalyst and supports the oxidation at the anode [122].

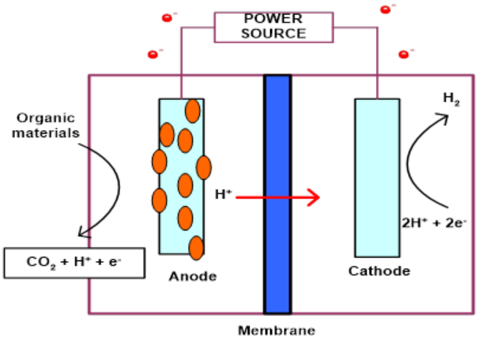

Figure 12. MEC for hydrogen production.

Shen *et al*. [123] have presented the MEC technology for wastewater treatment and generating hydrogen. The present investigation provides evidence that treating swine waste with a MEC can be a successful method for recovering H_2. Although adjustments in the flow rate showed an insignificant effect on system performance, raising organic loadings and applied voltages had a favorable impact. Huang *et al*. [124] used an integrated reactor to combine anaerobic digestion (AD) and single-chamber MEC treatment in order to recover hydrogen from food waste (FW) effectively. In the AD-MEC, the hydrogen recovery rate was found to be 96%, and the electrical energy recovery rate was 238.7%, respectively. Chavan and Gaikwad [125] presented using lignocellulose to produce hydrogen via successive enzymatic treatments and microbial electrolysis via MEC. In this study, the performance of MEC was done by introducing iron oxide nanoparticles (IONPs) to an anode. Compared to the MEC with an uncoated anode, hydrogen production efficiency was 1.14 times higher. A dual-chamber MEC with concentric cylinders was reported by Zhang *et al*. [126] to produce hydrogen. The maximum proportional hydrogen yield was 2.46 mmol/L/D, and energy recovery efficiencies were 215.33%.

The main advantages and disadvantages of the above-mentioned biological methods are presented in Table 4.

Table 4. Main advantages and disadvantages of biological methods.

Methods	Advantages	Disadvantages
Fermentation	The hydrogen production is enhanced via the alternating and complementing of photo and dark fermentation methods.	The formation of side products in dark fermentation leads to poor yield of hydrogen. The photofermentation process needs a sufficient supply of ATP.
Biophotolysis	In direct biophotolysis, water, and sunlight are needed for the generation of hydrogen. The high selectivity for hydrogen in indirect biophotolysis is a major advantage.	Direct biophotolysis requires high light intensity. Oxygen can decrease the photochemical efficiency. In indirect biophotolysis, the hydrogenase enzyme reduces hydrogen yield.
Electrochemical	The MEC system can easily be modified as a requirement. Hydrogen yield is high.	An external power supply is required. Requirement of catalysts for electrodes.

4. Conclusions

Hydrogen is considered a green fuel. Water is produced when hydrogen is used as a fuel, and it can be recovered to produce more hydrogen. The energy produced from biohydrogen offers the primary advantage of avoiding releasing greenhouse gases while transforming hydrogen into energy. The insufficient yield and high production costs of current hydrogen production technologies need some advancement. The present study has summarised all biomass-based methods for producing hydrogen with updated work. This article will help select adequate and corresponding biomass for hydrogen conversion techniques.

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Conflicts of Interest

The authors declare that they have no conflict of interest in the publication of this article.

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