REVIEW ARTICLE

A review on biohydrogen production through photo-fermentation of lignocellulosic biomass

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Abstract
Photo-fermentation biohydrogen production is an eye-catching and environmentally friendly route that can be excellently performed at ambient conditions. Nevertheless, light conversion efficacy and photo-fermentation hydrogen production performance are still low, and hence, numerous approaches are explored to enhance biohydrogen production. This review is intended at describing comprehensive characteristics and general mechanism of photo-fermentation biohydrogen production and highlights the advantages of this approach over other methods. Moreover, various pretreatment procedures of potential lignocellulosic biomass feedstocks for enhanced photo-fermentation biohydrogen production including physical, chemical, physical-chemical, and biological methods were elaborated thoroughly. Several crucial factors affecting photo-fermentation biohydrogen production such as the impact of pH, mixing, stirring, and lighting conditions, substrate concentration, different pretreatment conditions, and diverse fermentation modes were also discussed comprehensively. This aims to emphasize the recent advances in this field for further enhancement of biohydrogen production via photo-fermentation of lignocellulosic biomass. Additionally, the major challenge and prospects are also included to uncover the unexplored criteria of an effective and greener photo-fermentation biohydrogen production.

Keywords Biohydrogen production · Photo-fermentation · Lignocellulosic biomass · Eye-catching · Light conversion

1 Introduction

Nowadays, certifying energy safety is a crucial task for economic and political asset in the world. The increasing worldwide populations and demands of energy have resulted in a speedy rise in fossil fuel consumption [1]. It is well noted that other than the depleting source problem of fossil fuel, its widespread use has also led to global warming and the greenhouse effect due to the emissions of CO_2, CH_4, and N_2O, which could simultaneously affect human health and damage the ecosystem [2]. The upsurges of these greenhouse gases (GHGs) in the atmosphere have also led to climate change, increased surface temperatures, and thermal expansion of the seawater, thus raising the sea level, as well as the melting of glaciers and ice sheets [3]. However, the global reliance on these conventional energy sources of fuel for energy production is at a crucial level nowadays. In this respect, the search for alternative clean renewable sources of energy is critically developed.

Among various renewable energies explored to substitute fossil fuel, hydrogen has received incredible attention due to its greener production technology, high content of energy, and also its ability in giving considerable economic, environmental, and social credentials [4]. Besides, hydrogen has a higher ignition ability and could selectively reduce carbon emission [5]. As a clean fuel, hydrogen combustion only generates water, and thus, hydrogen has become a promising tool to overcome the global warming effect and reduce the air contamination problem [6]. The calorific value of hydrogen gas is ~ 3042 cal m^{-3} with the largest gravimetric energy density and, hence, can be extensively utilized as a transport fuel and for electricity generation [1]. Besides, hydrogen could encounter 18% of the energy request by reducing 6 Gt of CO_2 releases per annum by 2050. It is also expected that in that year, about 20–25% of the transportation industry involving over 15–20

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million lorries, almost 5 million buses, and 400 million cars will be powered with hydrogen [7]. Moreover, other than its use as an alternative fuel, hydrogen is also widely used in various industrial processes such as the glass industry, the thermal treatment of metals, and so on [8]. Therefore, based on its environmental and economic values, hydrogen-based systems are anticipated to function at greater efficacies soon.

To date, the worldwide demand for hydrogen has roused demonstratively and is estimated to provide around 10% to the entire energy market by 2025 [9]. Hydrogen production can be divided into two types, which are hydrocarbons reforming and non-hydrocarbon reforming (Fig. 1). Precisely, the hydrocarbons reforming is composed of a dry reforming, steam reforming, auto-thermal reforming, and partial oxidation processes [10]. As one of the mitigating greenhouse emissions strategy and addressing energy problems, the use of greenhouse gases to generate value-added chemicals of fuels has become the main focus of research nowadays. The CH_4 and CO_2 are reasonably economical carbon sources due to their natural profusion, and they also are the main compounds of renewable resources such as landfill gas and biogas [11]. Nonetheless, despite their promising performance in hydrogen production, all the abovementioned hydrocarbons reforming processes generally involve the steaming or transformation of coal or hydrocarbons, which inevitably also upsurge the utilization of fossil fuels and led to the greenhouse gas effect.

To encounter the demand for hydrogen without using the non-environmental friendly fossil fuel, the economical and greener production of hydrogen via non-hydrocarbons reforming has become an essential part of the hydrogen economy. Hence, hydrogen production from clean energy sources and auspicious hydrogen technologies for large-scale production has become a worldwide interest nowadays. There are several alternative hydrogen productions from non-hydrocarbons sources that have been reported so far, which include the use of water electrolysis, thermolysis and thermochemical water splitting, biochemical, and photonic energies. The water electrolysis can be performed using two electrodes in water, and by passing the electrical current, water is transformed into hydrogen and oxygen. This method is further divided into the electrolyte alkaline, proton exchange

membrane (PEM), and solid oxide electrolyzer (SOE) [10]. At present, electrolyte alkaline or also known as alkaline water electrolysis (AEL) is the most established electrolysis technology and it is commonly used for large-scale hydrogen production [12]. In a usual alkaline electrolysis cell, two Ni-based electrodes were immersed in a liquid electrolyte containing a 30–35-wt% aqueous potassium hydroxide (KOH) solution that was parted by a porous diaphragm. The electrolysis process was conducted at a temperature between 60 and 90 °C and the pressure below 30 bar. This approach could successfully produce high purity of hydrogen (99.5–99.9%), which can be augmented up to 99.999% by catalytic gas purification. The main advantage of this technology is its obtainability and more economical method than other electrolysis technologies.

Recently, the PEM electrolyzer has emerged as a promising hydrogen production technology due to its capability to couple with wind and solar energy resources, using environmentally friendly electrolytes, lesser power obligation, higher current density and hydrogen purity, and more available hydrogen storage [13]. During the reaction, the oxidation of water is occurred at the anode, thus generating oxygen, electrons, and protons. The protons and electrons are transferred to the cathode through the PEM, and finally, the hydrogen gas is produced at the cathode after the reduction of protons [10]. Despite its important criteria as an exciting pathway of synthesizing zero carbon footprint hydrogen, this technique requires the use of the expensive noble metal, which has limited its application range to some extent. On the other hand, the SOE has received increasing attention in recent years due to the unique advantages including high conversion efficiency and high purity hydrogen production rate [14]. Moreover, the high operating temperature evades the use of noble metal-based catalysts that is necessary for PEM technology, and this approach also allows the exploitation of numerous waste heat sources [15]. Notwithstanding these advantages, the inadequate long-term durability has prohibited the commercialization of SOE.

Thermolysis and thermochemical water splitting can be seemed as similar techniques, regardless of the high-temperature source. The thermolysis process is a direct thermal decomposition of water to hydrogen and oxygen at a very
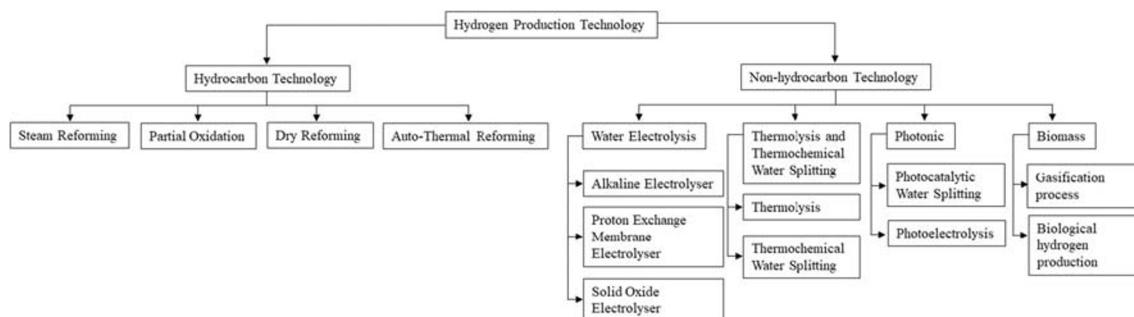

Fig. 1 Hydrogen production technology [10]

high temperature, while the thermochemical process involves the chemical reactions and the heat transfer processes [10]. On the other hand, the photonic process includes the use of photon energy for hydrogen production and it could be further categorized into photocatalytic water splitting and photoelectrolysis. The photocatalytic water splitting hydrogen production has gained increasing scientific attention due to its simplicity and environmentally friendly technique [16]. Numerous materials have been established for this process over the past few decades. Among them, titanium dioxide (TiO_2) is the most widely used material because of its physicochemical constancy and ideal water splitting potential. In contrast, photoelectrolysis hydrogen production is a similar process to electrolysis. However, it involves the direct use of light by the transformation of solar energy into electrical current and, finally, the conversion of water into hydrogen [17].

Biomass gasification hydrogen production is a thermochemical process for the destruction of feedstocks to produce hydrogen energy [18]. This method is composed of steam gasification and supercritical water gasification processes [19]. The biomass steam gasification comprises the transformation of raw biomass materials into combustible gases of H_2, CO, CO_2, CH_4, and hydrocarbons. It could be conducted at a high temperature assisting by the presence of water vapor as a gasification agent. In contrast, the supercritical water gasification is the hydrothermal process in a liquid water processing medium, when the properties of the liquid and gaseous phases present above the critical point. In this process, biomass can be disintegrated by hydrolysis, pyrolysis, condensation, and dehydrogenation to generate H_2, CO, CO_2, CH_4, and other gases.

As part of biomass technology, the generation of hydrogen from biological sources, which is also known as biohydrogen, has gained countless interest, mainly due to its slightest environmental effect. Recently, widespread research has been performed worldwide to enhance biohydrogen production as a substituent to avoid the use of fossil fuels for energy production. As previously mentioned, the use of fossil fuels for hydrogen production could inevitably lead to the greenhouse gas effect and depletion of fossil fuel sources. Besides, the activation of methane for hydrogen production is also a challenging task, due to the presence of sp3 hybridization of the atomic orbitals of carbon that makes the carbon-hydrogen bonds in methane very strong [20]. On the other hand, as a multicomponent mixture, liquid fuels are comprising a huge number of hydrocarbons, including naphthenes, paraffins, aromatics, olefins, and sulfur compounds [21]. Due to the mixed nature of this fuel, there are several technical issues to the reforming process, such as the deactivation of catalytic active sites by the presence of sulfur compounds and the deposition of carbon on catalytic surfaces under reforming conditions [22]. In contrast, as an important feedstock for biohydrogen production, lignocellulosic biomass is considered a plentiful and renewable resource. To date, the worldwide, the manufacture of lignocellulosic biomass is about 120×10^9 tons per annum, which is equivalent to 2.2×10^{21} J, 300 times higher than the current global energy demand [23]. The use of lignocellulosic biomass prevents the competition with food production or animal feed, and as a carbon-neutral substrate, it is an environmentally friendly resource [24]. Therefore, the exploitation of lignocellulosic biomass can be a probable roadmap to cultivating an environmental, sustainable, and economical hydrogen production technology.

Recently, many studies have been carried out to search for an active and selective condition for increased biohydrogen production rate and yield. Remarkably, many previous outstanding reviews and viewpoints discussed general hydrogen and biohydrogen production, dark fermentation process, and other biohydrogen generation routes. However, to the best of our knowledge, the review on photo-fermentation biohydrogen production as one of the capabilities approach is still scanty, even for the fact that in recent times, intensive research efforts have been made to reveal the vital aspects related to that technique. Thus, the current literature is hoped to contribute a better insight into the design and development of an efficient photo-fermentation process of lignocellulosic biomass for improved biohydrogen production.

2 Biohydrogen production routes

Generally, the biohydrogen production route can be categorized into various routes such as bio-photolysis including direct and indirect photolysis, microbial electrolysis, and fermentation such as dark and photo-fermentation, as well as a hybrid system. It is worth mentioning that each technique has its benefits and difficulties according to feasibility, sustainability, and energy effectiveness. In biohydrogen production, numerous organic substrates and microorganisms have been used in the different biological route. It is noteworthy that the manipulation of those substrates and microorganisms for hydrogen production not only has a dual effect of waste elimination but also led to an economic profit of energy production and waste clearance costs [25]. Various processes for the generation of biohydrogen are simplified in Fig. 2. In general, there are two processes in biohydrogen production from microalgae which are the light-independent and light-dependent processes. In the first process, microalgae biomass that is rich in carbohydrate and protein is used as a feedstock [26]. This process can be further categorized into dark-fermentation and microbial electrolysis cells [4]. Meanwhile, for light-dependent, the system is quite similar to photosynthesis and composes of photo-fermentation and bio-photolysis. The latter process could be further categorized into two different processes which are direct and indirect bio-photolysis. In this review, the main focus will be on photo-

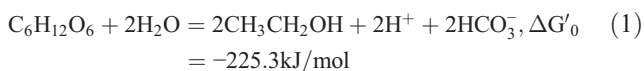**Fig. 2** General scheme of various processes for biohydrogen production
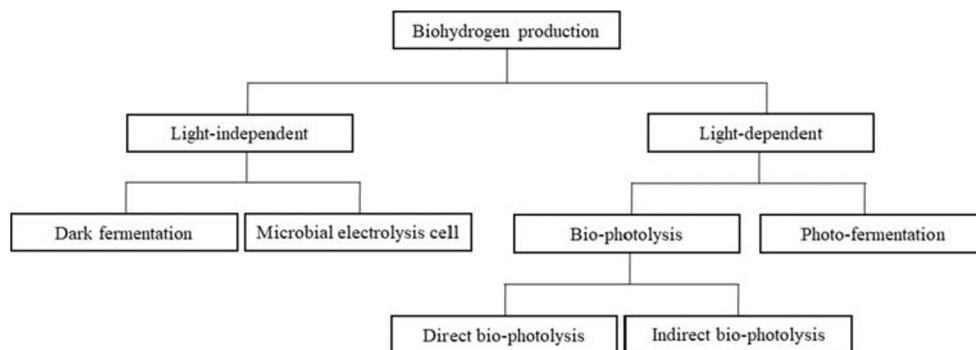
fermentation; however, a general discussion on other related methods will be included in the next sections to provide a fair comparison between those methods.
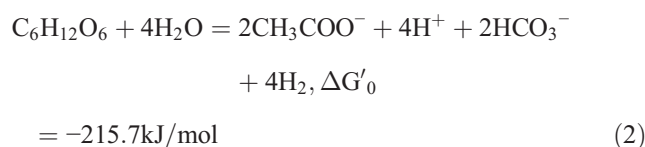
2.1 Dark fermentation

A conversion process of biological resources into energy by consuming microorganisms assisted by nitrogenases or hydrogenases and enzymes is known as fermentation [5]. A less energy demanding and a simple approach for biohydrogen production are known as dark fermentation (DF). Even though this process is a traditional technique, it is still an auspicious technology that can reduce the sludge, inoffensiveness, and energy or nutrients including hydrogen and short-chain fatty acid recovery that have been instantaneously attained [27]. In this process, hydrogen, CO_2, and volatile fatty acids are produced via abundant carbohydrates originated from the food and paper industry, agricultural, municipal wastes, etc. by microorganisms. This method also provides a good impact to waste removal, since many countries officially forbid the direct disposal area for organic wastes containing energy [28].

In DF, two possible pathways might involve. Generally, glucose is first transformed into pyruvate via the glycolytic pathway. Then, adenosine diphosphate (ADP) and the reduced nicotinamide adenine dinucleotide (NADH) generate adenosine triphosphate (ATP). In the first case, under anaerobic conditions, pyruvate is transformed into carbon dioxide and acetyl coenzyme A (acetyl-CoA) that catalyzed through pyruvate–ferredoxin oxidoreductase (PFOR). Differently in facultative anaerobes (aerobic condition), pyruvate formate lyase (PFL) catalyzes the transformation of pyruvate to formate and acetyl-CoA. In both cases, however, acetyl-CoA is lastly transformed into ethanol, acetate, or butyrate, subject to the used microorganisms and the environmental conditions [29]. The metabolic routes through ethanol, acetate, and butyrate are presented in equations below [30];
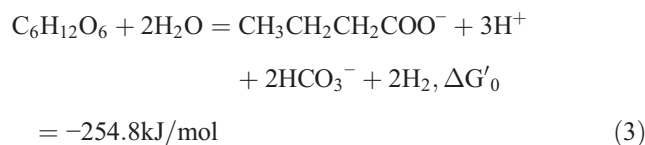
Ethanol pathway:

$$C_6H_{12}O_6 + 2H_2O = 2CH_3CH_2OH + 2H^+ + 2HCO_3^-, \Delta G'_0 \quad (1)$$
$$= -225.3 kJ/mol$$

Acetate pathway:

$$C_6H_{12}O_6 + 4H_2O = 2CH_3COO^- + 4H^+ + 2HCO_3^-$$
$$+ 4H_2, \Delta G'_0$$
$$= -215.7 kJ/mol \quad (2)$$

Butyrate pathway:

$$C_6H_{12}O_6 + 2H_2O = CH_3CH_2CH_2COO^- + 3H^+$$
$$+ 2HCO_3^- + 2H_2, \Delta G'_0$$
$$= -254.8 kJ/mol \quad (3)$$

2.2 Microbial electrolysis cell

In recent years, microbial electrolysis cell (MEC) has been established as a novel anaerobic digestion reactor for biohydrogen production. This technique has also emerged as an encouraging technology for the conversion of organic matter into higher hydrogen yields [31]. Among various organic matters, volatile fatty acids (VFAs) and monosaccharides are the momentous carbon compounds in lignocellulosic hydrolysate or wastewater that can be converted to hydrogen in MEC [32]. The main advantage of this method is its capability in overcoming the fermentative obstacle in the fermentation-based processes and produce a high yield of hydrogen [33]. Besides, this approach possesses an enormous substrate diversity and minimal energy input, as well as environmentally sound than other biohydrogen production methods. In general, the MEC converts organic compounds into valuable hydrogen energy using low additional voltage (< 1.23 V) and electrogenic species of microorganisms [34]. In MEC, thermophiles or extremophiles microorganisms play a very significant role in hydrogen production together with the appropriate electrode material. Commonly, carbonaceous resources including carbon cloth, carbon brush, carbon paper, and graphite are among the potential electrodes in MEC.

Principally in MEC, the anaerobic bacteria that are present on the anode will consume organic matter and convert it to

hydrogen gas, and this process is known as electrohydrogenesis [35]. These anaerobic bacteria are frequently denoted as anode-respiring bacteria (ARB) that are capable to transfer electrons to a solid electrode from a biodegradable substrate [36]. The working principles of MEC are illustrated in Fig. 3. The major side products of ARB metabolism are CO_2, electrons, and protons, which then are transported to the anode before being flowed to the cathode via an external circuit. Then, electrons flow freely and join protons via an electrical load where the hydrogen gas is produced. However, to successfully yield hydrogen from the combination of these electrons and protons at the cathode, an external voltage (≥ 0.2 V) should be supplied to MEC reactors under a biologically aided condition of $P = 1$ atm (1.01×10^5 Pa), $T = 30$ °C, and pH = 7 [37].

Despite its abovementioned advantages, there is some limitation in this method that has been highlighted in the previous study, which is the probability of the hydrogen formed being effortlessly scavenged by methanogens, homoacetogens, and even exoelectrogens in the single-chamber [31]. This has led to an inhibited hydrogen production efficiency of MEC. However, increasing numbers of researches have been dedicated to overcoming those shortcomings and consequently enhance the MEC for hydrogen production.

2.3 Bio-photolysis

Bio-photolysis is a photonic-driven biohydrogen production, and it is a very common approach using cyanobacteria and blue-green algae by operating based on a similar principle as photosynthesis in plants. This process can be further categorized as direct bio-photolysis and indirect bio-photolysis [38]. The direct bio-photolysis involved the photosynthesis, in which algae and cyanobacteria break the water into hydrogen and oxygen (Fig. 4a) [40]. Photosystem I (PSI) and photosystem II (PSII) as the photosynthetic reaction sites in the chloroplasts of microalgae could absorb photons to produce a strong oxidant for the oxidation of water into O_2, electrons, and protons. Hydrogen is formed upon the reduction of a proton by an electron which is provided by reduced ferredoxin (Fd) of the hydrogenase enzyme that exists in the cells [39]. It is worth mentioning that the H_2 production in blue-green algae is primarily due to [FeFe] hydrogenase enzyme that is highly O_2 sensitive, which has been recognized as the main bottleneck of algae photolysis H_2 production [41]. Thus, in this
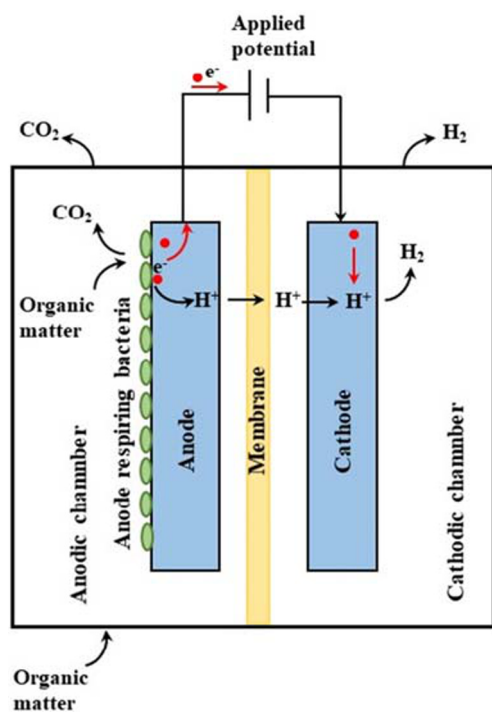

Fig. 3 Schematic of typical two-chamber MEC for biohydrogen production [36]
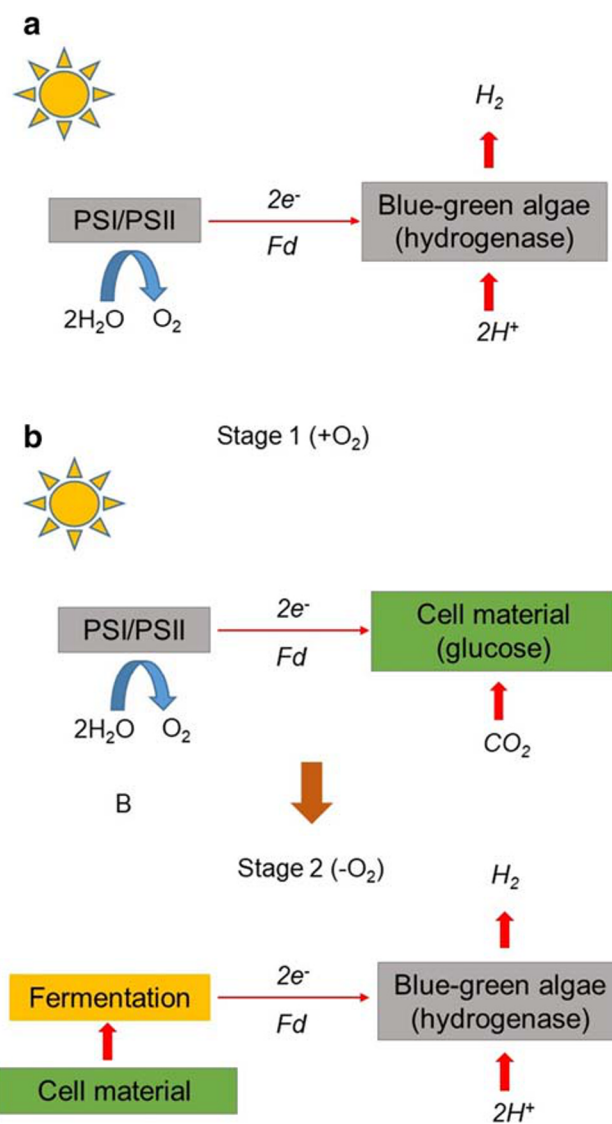

Fig. 4 Schematic representation of a direct biophotolysis and b indirect biophotolysis for biohydrogen production [39]

process, H_2 evolution occurs for a temporary period upon illumination, before the hydrogenase gets deactivated by the accumulated O_2 [26]. For that reason, several approaches have been taken to reduce O_2 levels during hydrogen production for enhanced performance including the addition of an oxygen scavenger, purging the inert gases to the reaction mixture, and reduction of sulfur in the cultivation media.

In contrast, CO_2 fixation and accumulation of carbohydrate occurred firstly during photosynthesis for indirect biophotolysis, followed by fermentation of the carbon reserves which leads to hydrogen production as follows:

$$12H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \tag{4}$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2 \tag{5}$$
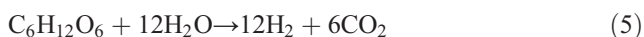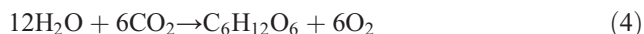
Via this process, cyanobacteria and microalgae can yield H_2 from stowed glycogen, and this method has solved the O_2 sensibility issue by impermanently separating the H_2 and O_2 evolution into two distinct steps via CO_2 evolution or fixation [26]. The detail of this process is illustrated in Fig. 4b. During the early stage, microalgae are permitted to cultivate under standard cultivation environments (aerobic phase) to form lipids, carbohydrates, and other organic molecules by transforming solar energy and via CO_2 fixation. The electron transfer chain stops upon O_2 depletion are attained and the second step started (anaerobic phase). In PSI, the formed electrons of endogenous substrates from catabolism in the citric acid cycle and glycolytic pathway are used to non-photochemical reduce the PQ pool via light-dependent Fd reduction. Finally, hydrogen is produced after electrons were transferred to [Fe-Fe] hydrogenases.

3 Photo-fermentation

Biohydrogen production via photo-fermentation using photosynthetic bacteria was first recognized by Gest and Kaman in 1949, and since then, this technology has shown an effective production of high purity hydrogen without the generation of oxygen [42]. In photo-fermentation, biohydrogen is produced via nitrogenase-catalyzed reaction during the decomposition of organic compounds in the presence of light energy by photosynthetic bacteria or anaerobic bacteria strains, including *Rhodobium*, *Rhodobacter*, *Rhodospirillum*, and *Rhodopseudomonas* [43]. Due to its main benefits of broad raw material resources and comprehensive substrate consumption, photo-fermentation hydrogen production has become world-wide main research nowadays [44]. Besides, this process is very efficient, environmentally friendly, and can generate large-scale hydrogen at ambient temperature and pressure. The photo-fermentation reaction can be described as follows:

$$C_6H_{12}O_6 \rightarrow 6CO_2 + 12H_2 \quad \text{(Photosynthetic bacteria)} \tag{6}$$

In typical photo-fermentation, a photo-reactor with appropriate volume is put in the incubator with fixed light intensity for hydrogen production experiments [45]. Firstly, photo-fermentation broth containing several amounts of a substrate, inoculum, and medium was added to the photo-reactor. Before the fermentation process, the preliminary pH in the photo-reactor was set up at an optimized condition. In this case, the pH levels were attuned by the addition of 5 M NaOH or 5 M HCl [46]. Then, the photo-reactor was purged for 5 min with nitrogen or argon to preserve oxygen-free conditions [47]. Usually, the temperature was maintained at 30 °C, which is based on the previously reported study [42]. Then, the hydrogen production was performed under constant stirring for several days with a sampling interval at 12 h. For the collection of hydrogen, a specific bag was utilized, and finally, a gas chromatograph was used to measure the hydrogen concentration. The schematic diagram of hydrogen production via photo-fermentation is illustrated in Fig. 5.

In photo-fermentation biohydrogen production, several difficulties have been identified. For instance, photosynthetic bacteria have limitations in capturing the sunlight's energy that might lead to a very low light transformation effectiveness to biohydrogen production [49]. These bacteria also require suitable sterile and environmental conditions for their growth and to generate hydrogen [50]. Moreover, due to the high amount of activation energy, high-energy demand is required by nitrogenase enzymes to perform the photo-fermentation process. Besides, the cell shadowing effect also decreases the light penetration inside the photoreactor and consequently decreases the light intensity for a reduced biohydrogen production performance. In terms of a large-scale application, a huge land coverage area is essential to realize an efficient anaerobic photobioreactor.
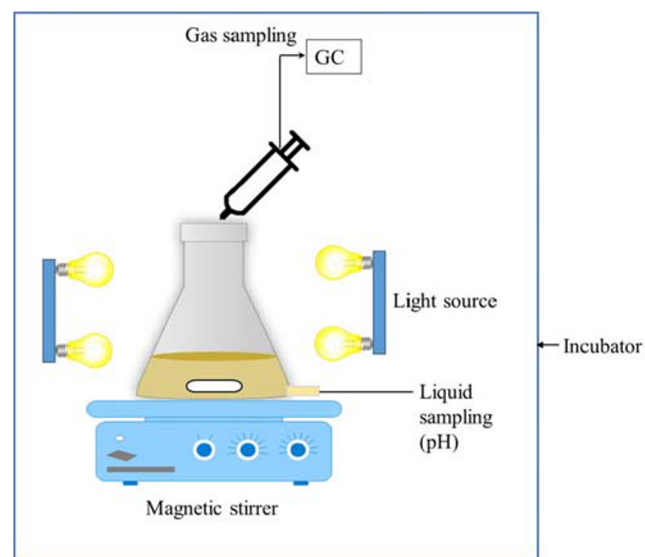

Fig. 5 Schematic diagram of photo-fermentation bioreactor [48]

3.1 Potential feedstocks of photo-fermentation biohydrogen production

To date, the use of organic substrates for hydrogen production is an eye-catching idea for emerging sustainable and renewable technologies. As one of them, biomass is an organic material that originates from animals and plants, and it is a renewable source of energy. Among numerous biomass resources, lignocellulosic biomass is the most flexible material that can be used for biohydrogen production at a large scale due to its high cellulosic content, enormous accessibility, and renewability [51]. Even though lignocellulosic biomass was frequently considered as a valueless raw material that should be disposed of as waste, numerous research groups are recently pursuing to convert lignocellulosic biomass into new value-added products [52]. Lignocellulosic biomass can be further categorized into several types, including energy crops, agricultural residues, forestry waste, forestry, industrial and domestic waste, algae, and any other animal manure (Fig. 6). It is worth noting that these resources considerably vary in the structures, compositions, and contents [53].

Specifically, lignocellulosic biomass is further composed mainly of hemicellulose, cellulose, and lignin [54]. Cellulose is a homogeneous polymer that consisted of glucose or six-carbon sugars. Cellulose and its derivatives are the supreme plentiful biopolymers on earth and the most extensively studied renewable materials, which are present in cotton, wood, hemp, and other plant-based materials that act as the main strengthening material in plant structures [55]. Meanwhile, hemicellulose is a mixture of heterogeneous polysaccharides with assorted structures that consisted of five-carbon sugar sub-units, including mannose, arabinose, and xylose [56]. Hemicellulose polysaccharides are easily soluble in alkalis and simply hydrolyzed or devolatilized by dilute base or acid. On the other hand, lignin as the most plentiful phenolic polymers naturally produces ether or ester linkages with hemicellulose accompanied by cellulose and thus builds a valuable and complex lignocellulose polymer [57]. Besides, lignin possesses a complicated cross-linking structure consisting of numerous functional groups such as aliphatic hydroxyl, methoxyl, and phenolic hydroxyl groups. It is worth mentioning that these functional groups especially the hydroxyl and aromatic structure crucially impact the chemical properties and reactivity of lignin. Despite the wide consumption of these resources, the development of pretreatment methods is essential to break up the lignin structures to isolate the three biopolymers (lignin, cellulose, and hemicellulose) and improve enzyme digestibility of cellulose [58].

3.2 Pretreatments of lignocellulosic biomass for photo-fermentation

Various pretreatment approaches of lignocellulosic biomass have been performed so far before biohydrogen production. These steps are crucial to increase the production of sugars and evade the loss or degradation of carbohydrates, as well as the generation of inhibitory products for consequent conversion processes which are hydrolysis and fermentation. It is well noted that the sustainability of the biohydrogen economy prominently depends on the economical production of
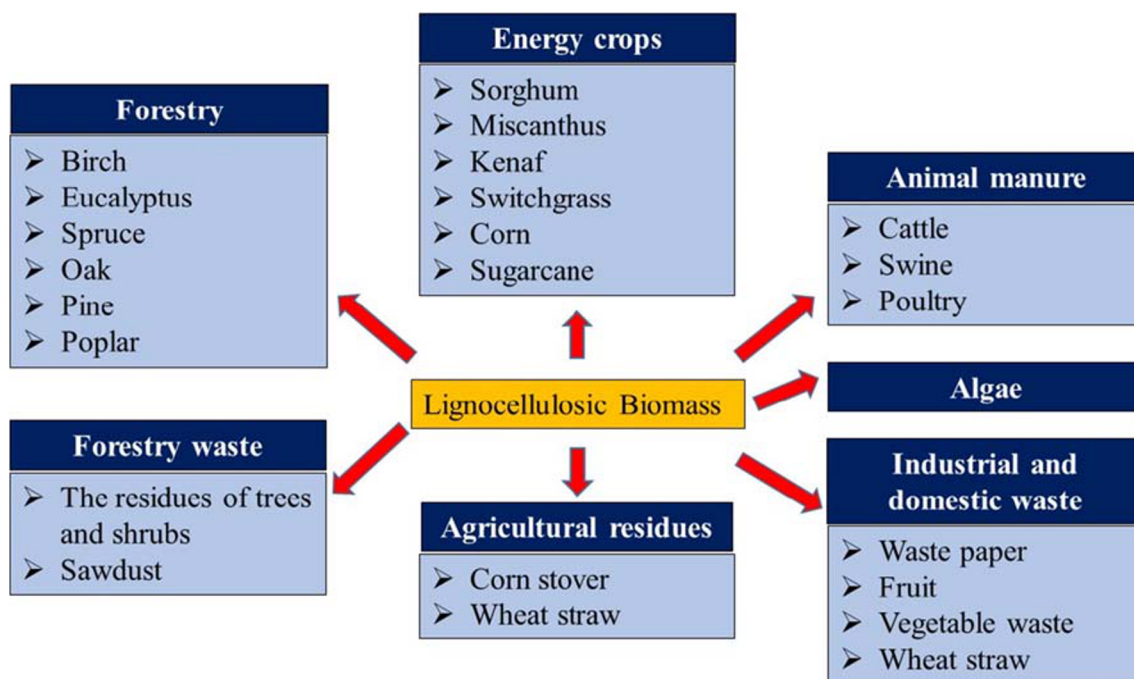

Fig. 6 Different types of lignocellulosic biomass [53]

hydrogen and the easy accessibility of substrates. Therefore, a combination of hydrogen production with the treatment of ample biomass leftover and wastewater substrate is one of the auspicious approaches to competently accomplish this purpose [59]. A promising pretreatment step should possess a low operating cost, low capital, efficiency on a broad range of lignocellulosic biomass, as well as could excellently recuperate most of the lignocellulosic components [60]. Generally, the pretreatment processes for biohydrogen production can be categorized into chemical, physical, biological, and physical-chemical methods. However, in this study, the main focus will be on several pretreatment techniques involved in biohydrogen production via the photo-fermentation method. The selected pretreatment approaches of several lignocellulosic biomasses for photo-fermentation are simplified in Table 1.

Explicitly, the physical treatment methods could be further classified into mechanical and irradiation types. For mechanical treatments, it involves milling, grinding, cutting, shearing, chipping, etc. Among them, milling and grinding are the most commonly used on lignocellulosic biomass to reduce the size and consequently upsurge the available surface area for the reaction [60]. These methods should be applied before the biomass is exposed to any other pretreatment, as it has been shown that adequate particle size can prominently increase the biohydrogen production [66], while diverse types of radiation, including microwaves, ultrasounds, gamma rays, and electron beams, could enhance the liquefaction of the wastes, thus enhancing the effectiveness of the bioprocesses [67]. For instance, the glycosidic bonds in the cell wall of the biomass will be broken upon exposed to gamma rays, hence leading to cell disruption. On the other hand, irradiation under an electron beam could depolymerize and splits cell walls composing lignocelluloses of the wastes.

In 2017, about 2.01 billion tons of urban solid waste was globally produced, and it has been expected that this waste production will upsurge to 3.40 billion tons by 2050. It was also reported that the indecorous management of organic leftovers such as food waste and yard waste could contribute to numerous environmental problems, such as ecosystem destruction, climate change, and resource reduction [68]. For that reason, the conversion of those wastes to energy has recently gained the interest of many researchers. Typically, food wastes are ample and possess high carbon content that is suitable as renewable substrates for biohydrogen production [69]. Food wastes compose of a small amount of lignin; therefore, for their transformation to biohydrogen, very little or no pretreatments are essential, as compared with forest and agricultural residues [61].

As one of the food wastes, bread and bakery product wastes were selected as a substrate for biohydrogen production [61]. The goal of this work was to transform bread

Table 1 The combined pretreatment methods for photo-fermentation biohydrogen production

Substrate	Pretreatment methods	Operation mode	Bacteria	Findings	References
Bread waste	Milling and drying	250 mL round shaped bottles, 25-28 °C, pH 6.8, light intensity of 40 W/m² for 8 days	R. palustris	3.1 mol H_2/mol glucose	[61]
Giant reed	Alkaline treatment and enzymatic hydrolysis	150 mL flask, 30 ± 1 °C, pH 4.8, 2000 lux for 72 h	HAU-M1 bacteria	98.3 mL H_2/g TS	[62]
Thermophilic/dark fermentation effluent	Centrifugation, dilution, buffer addition, pH adjustment and sterilization	12–105 mL sealed glass bottles, 30–33 °C, pH 6.6–6.8, light intensity of 4000 lux	Rhodobacter capsulatus	1.0 L H_2/L$_{culture}$	[63]
Dark fermentation effluent	Enzymatic hydrolysis	150 mL glass reactor, 30 °C, pH 6.5, 3000 lux light intensity	Para clostridium, Enterococcus, Sporanaerobacter and Clostridium_sensu_stricto_1	1287.06 mL H_2/g TOC	[64]
Corncob	Milling and enzymatic hydrolysis	250 mL conical flask, 30 C, pH 6, 4000/7000 lux intensity of light	Rhodospirillum rubrum, Rhodobacter capsulatus, Rhodopseudomonas palustri	84.7 mL H_2/g TS	[65]
Potato residue	Drying, smashing and enzymatic hydrolysis	150 mL conical flask, 30 °C, pH 5–9, 3000 lux intensity of light	Rhodospirillum rubrum, Rhodobacter capsulatus and Rhodopseudomonas palustris	642 ± 22 mL H_2	[46]

wastes into hydrogen with a consecutive system composed of lactic fermentation and photo-fermentation, with the least number of treatments to the substrate. The first stage involved the lactic fermentation to attain the organic acid, followed by photo-fermentation of that organic acid in the second stage. Before the reaction, bread wastes were dried in an oven at 60 °C for overnight, ground, and kept at − 20 °C in 100-mL flasks before horizontally shaken for 24 h at 100 rpm. This material was retained at certain temperatures to establish a favorable temperature. The period of the fermentation was optimized at the selected temperature. Then, lactic acid concentration and pH were measured after several sampling in 48 h. Before hydrogen production, the consecutive clambering up was performed in the bigger flasks (3 L) at optimized temperature and stirring conditions. During the hydrogen production experiment, *R. palustris* was inoculated into the medium obtained from 3 L production sets. Two hundred and fifty-milliliter round-shaped bottles were employed as the reactors, and the subsequent conditions were examined: the existence or non-appearance of smaller bread pieces within the medium and the addition of nutrients such as magnesium sulfate, ferric citrate, and *p*-amino benzoic acid (PABA). The results showed that for the former condition, the existence or non-appearance of smaller bread pieces had no significant influence on *R. palustris* activity. Meanwhile, the addition of ferric citrate and magnesium sulfate improved hydrogen production (102.71 ± 3.82 mL H$_2$), compared with only ferric citrate addition (89.20 ± 0.01 mL H$_2$), while an additional supplement of PABA did not further increase the hydrogen productivity (99.97 ± 1.96 mL H$_2$).

In contrast, the chemical pretreatment techniques involve the use of acid, alkali, solvents, and oxidizing agent to disintegrate and saccharification the cell wall of the carbohydrates. Among those approaches, the acid and alkali reagents, combined with heat, are usually utilized for the solubilization of organic matter [26]. Besides, there are also several types of research on a combination of chemical treatment with enzymatic hydrolysis. For instance, Jiang and co-workers have utilized *Arundo donax* L. or giant reed as a feedstock for photo-fermentation biohydrogen production [62]. Generally, the giant reed is a perpetual rhizomatous grass and an auspicious energy crop due to its easy adaptation to different types of weather and soil conditions, high biomass yield, lesser cultivation prerequisite, and phytoremediation criteria [70]. Before biohydrogen production, alkaline pretreatment of giant reed was carried out using Ca(OH)$_2$ and NaOH [62]. During the process, 200 mL of Ca(OH)$_2$ and NaOH with different concentrations (1–20 (g/L)) were used, while the loading ratios were 1–20% (g alkali/g TS of giant reed biomass), respectively. Then, the Parafilm-covered flask was incubated for 24 h at room temperature and washed with tap water to attain pH 8 before 1 M HCl was used to reach pH 7.0. Finally, the giant reed was dried and ready for additional treatment by enzymatic hydrolysis before the photo-fermentation reaction. It was observed that the giant reed pretreated with 20% NaOH obtained 98.3 mL/g TS of hydrogen yield, a 20% higher than that of pretreated with Ca(OH)$_2$ (78.6 mL/g TS) under optimal condition. This could be explained by the fact that the NaOH and Ca(OH)$_2$ pretreatments would enhance the porosity and internal surface area and decrease polymerization and crystallinity after lignin-carbohydrate linkages cleaving. As a result, the sugar yield from enzymatic hydrolysis and hydrogen yield from photo-fermentation would also be directly impacted. Even though both NaOH and Ca(OH)$_2$ solutions were used under the same amount, the poorly soluble of Ca(OH)$_2$ in water has led to less effective hydrogen production compared with NaOH pretreatment.

Meanwhile, the combination of both physical and chemical pretreatment is known as the physical-chemical method. For instance, dark fermentation effluent (DFE) was used as feedstock for photo-fermentation using *Rhodobacter capsulatus* bacteria [63]. This effluent composes of the Miscanthus hydrolysate through *Thermotoga neapolitana*. The pretreatment steps that are involved before reaction are dilution, buffer addition, centrifugation, sterilization, and pH tuning. Each step was significantly impacted the biohydrogen production, in which centrifugation enhances the clearness of the effluent, dilution with water could decrease the concentration of organic acid, stabilization of the pH throughout photo-fermentation was done by buffer addition, and sterilization inhibits the impurity. Besides, the influence of iron, vitamins, and other exterior microelements on biohydrogen production was also inspected. It was observed that only iron could promisingly enhance hydrogen production from 0.3 to 1.0 L$_{H2}$/L$_{culture}$, whereas other trace elements and vitamins insignificantly played role in this reaction. This result is in agreement with the previous finding that reported on the growth delay and almost no hydrogen production in the defined medium in the absence of iron, verifying that iron is necessary for cellular functions and the hydrogen production [71].

Theoretically, the use of DFE for hydrogen production is more complex than pure sugars because of numerous factors such as strict environmental control, substrate inhibitions (NH^{4+}), a suitable concentration of acetic acid and butyric acid, and C/N [64]. It was previously reported that by adding additional organic matters into DFE can positively affect the photo-fermentation by reducing the interruption period of hydrogen production. Among them, the addition of a diverse type of extra sugars as a supplement into DFE could improve the hydrogen yield by restraining the inhibition of bacteria. Interestingly, the use of enzymatic hydrolysate of corn straw as a readily available supplement could reduce the production cost and it also possesses a high-quality carbon source for hydrogen production. The enzymatic hydrolysate can alter the composition of fermentation substrate and dilute hydrogen production inhibitors. However, the effect of an enzymatic

hydrolysate of corn straw supplementing DFEs for enhanced hydrogen production was reported for the first time in this study. As a result, the enzymatic hydrolysate addition increases the hydrogen yield from 312.54 to 1287.06 mL H_2/g TOC and maximum hydrogen production rate from 2.14 to 10.23 mL/h than that of the control group, which was conducted without enzymatic hydrolysate addition. Based on both studies on the use of DFEs, it could be concluded that the use of iron or enzymatic hydrolysate of corn straw as a supplement could comparably produce a high yield of hydrogen. However, in terms of cost and environmental aspect, the use of enzymatic hydrolysate of corn straw seems to be more eye-catching technology. It is suggested that more research works are needed to further search for a more natural source of supplement that can enhance biohydrogen production by maintaining a cleaner environment.

On the other hand, the main advantage of biological pretreatment approaches than other techniques are that it did not require high pressure or temperatures, also without the demand for chemicals, including alkalis and acids [67]. Furthermore, a biological method can avoid the formation of undesired products. In one of the research, this technique was utilized to treat the corncob, one of the agriculture wastes [65]. Firstly, the corncob was dried in air and ball milled to form a powder. Then, the particle size, moisture content, volatile solids (VS), total solids (TS), cellulose content, and hemicellulose content were analyzed before this material proceeded with chemical treatment. Next, several amounts of corncob powder were added with 0.5 M citric acid-sodium citrate buffer solution in conical flasks and hydrolyzed enzymatically using the cellulose. Then, the flask was shaken, sealed, and kept in a continuous temperature oscillator for 48 h during enzymatic hydrolysis at 150 rpm and 50 °C. This substrate is now ready for photo-fermentation hydrogen production reaction.

Besides, potato starch agriculture wastes were also treated by this biological technique [46]. The potato waste was firstly washed, dried, and ground to form a powder. This powder was kept in a sealed bag and located in a dry and cool place. Then, enzymatic hydrolysis was conducted in l-L conical flask using 50 g potato starch powders. This powder was diluted with citrate-sodium citrate buffer (pH 6.0) to attain a 10% (w/v) solid-to-liquid ratio. Then, the mixture was incubated at 80 °C and 150 rpm for 20 min in a shaker after the addition of 0.1 mL/g α-amylase enzyme. After centrifuged at 10,000 rpm for 10 min, the resulting supernatant was filtered to observe the reducing sugar content before photo-fermentation.

3.3 Factors affecting photo-fermentation for biohydrogen production

Biohydrogen production is a multifaceted process that needs several optimization phases to attain a defensible and economical process. It was previously reported that numerous factors could significantly influence biohydrogen production through photo-fermentation including pH, light intensity, stirring mode, substrate concentration, and pretreatment condition. Inspired by that, this section is wished to deliver insight and scrutinize some important key parameters involved in biohydrogen production of lignocellulosic biomass via photo-fermentation. The previous studies on photo-fermentation biohydrogen production are simplified in Table 2. The following paragraphs will discuss in detail the previous studies that are tabulated in Table 2.

As one of those studies, the influence of preliminary pH on photo-fermentation was investigated using starch agricultural leftover substrate [46]. In this work, the adapted Gompertz model was implemented while monitoring hydrogen yield with initial pH changing from 5 to 9. The Gompertz model is broadly used in biological aspects, and it is recurrently utilized to designate the growth of plants and animals, as well as the number of bacteria and cancer cells [78]. From the photo-fermentation reaction of starch as a carbon source, hydrogen was formed primarily via butyric acid and acetic acid metabolism pathways. The largest sugar consumption rate of 0.26 g/(L h), the highest hydrogen yield of ~ 642 mL, and the fastest hydrogen formation rate of 77.78 mL/(L h) were achieved at pH 7. In contrast, lower yield of hydrogen and slowest hydrogen formation rate were attained at another initial pH. This is possibly due to the excellent bacterial growth at pH 7; hence, more hydrogen is produced from huge numbers of reducing sugar. After biohydrogen formation, reducing sugar intake was maintained until 84 h at a lower level, before a little intake rate was observed at different pH. This is probably caused by the incomplete degradation of the substrate during the enzymolysis process that was performed under an acid environment.

In other studies, the influence of the buffer's initial pH on photo-fermentation of corn stalk was investigated in terms of biohydrogen production and its kinetic study [44]. Besides, the hydrogen production rate, by-product generation, and reducing sugar intake were assessed at pH 5 to 7. Principally, a buffer solution assists in preventing superfluous alkalinity or acidity of a mixture. In photo-fermentation, the buffer compound was typically added to sustain a stable pH range of the medium during the process [79]. Numerous buffer compounds have been utilized in photo-fermentation so far, including citric acid-sodium citrate [65], potassium phosphate [79], ferric citrate, and sodium sulfate [80]. In Guo and coworkers study, the preliminary pH of potassium phosphate buffer was varied from pH 5 to 7 before photo-fermentation [44]. From the results, it could be observed that the maximum hydrogen production rate (23.96 mL/h) was achieved at pH 6.5. Differently, the maximum hydrogen production rates were only 5.59 mL/h and 5.42 mL/h for pH 5.0 and 7.5, respectively. It was claimed that at lower initial pH values,

Table 2 Previous studies on photo-fermentation biohydrogen production

Substrate	Bacteria	Enzyme	Promoter	Targeted Parameters	Findings	References
Potato residue	*Rhodospirillum rubrum, Rhodobacter capsulatus and Rhodopseudomonas palustris*	α-amylase	Citrate–sodium citrate buffer	Different initial pH	642 ± 22 mL and 77.78 mL/(L h) H_2 at pH 7	[46]
Corn stalk	*Rhodospirillum rubrum, R. capsulata, R. pulastris, Rhodobacter sphaeroides, Rhodobacter capsulatus*	Cellulose liquid	K_2HPO_4 and KH_2OP_4 buffer	Different initial pH values of the buffer	23.96 mL/h H_2 at pH 6 of buffer	[44]
Alfalfa (*Medicago sativa* L.)	HAU-M1	Cellulase	Citric acid/sodium citrate buffer solution	Initial pH, substrate concentration, and cellulase loading	55.81 mL/g H_2 at pH 6.9, 31.23 g/mL substrate conc., and cellulase loading of 0.13 g/g	[72]
Corncob	*Rhodospirillum rubrum, Rhodobacter capsulatus, Rhodopseudomonas palustri*	Cellulase	Citric acid-sodium citrate buffer solution	Interaction of lighting and mixing	84.7 mL H_2/g TS	[65]
Corn stover	HAU-M1	Cellulase	Citric acid buffer	Different intermittent stirring	57.63 ± 1.75 mL/g VS	[73]
Brewery wastewater	*Rhodobacter sphaeroides*	-	K_2HPO_4, KH_2PO_4, $MgSO_4 \cdot 7H_2O$, NaCl, $CaCl_2$, yeast extract, ferric citrate, trace element, and vitamin	Various substrate concentration	0.69 mol H_2/L medium	[74]
Corn straw	*Rhodospirillum rubrum, Rhodopseudomonas capsulate, Rhodopseudomonas palustris, Rhodobacter sphaeroides and Rhodobacter capsulatus*	Cellulase concentrate	Citrate buffer	Pretreatment methods	137.76 mL H_2/g TS	[75]
Energy grass	*Rhodospirillum rubrum, R. capsulata, R. pulastris, Rhodobacter sphaeroides, Rhodoba*	Cellulase	Buffer	Different enzymolysis time	5.53 mL H_2/(h g TS)	[76]
Dark fermentation effluents	HAU-M1	Cellulase	NA	Influence of batch, semi-continuous and continuous mode	1386.22 ± 44.23 mL H_2/g TOC	[77]

the hydrogen formation capability of bacteria progressively augmented with the upsurge in preliminary pH. Conversely, for the higher initial pH, the hydrogen generation capability decreased when the initial pH increases. This is possibly due to the delay in the peak period of hydrogen production, signifying that the alkaline environment would negatively impact the capability of photosynthetic bacteria.

Alfalfa (*Medicago sativa* L.) is a common food crop that belongs to the perennial leguminous herb, which grows in a large area in the world [81]. As well as being used as food, alfalfa also can be transformed into energy carriers with high-energy density such as hydrogen, bio-ethanol, and methane. Lu and co-workers have studied the influences of preliminary pH, cellulase loading, and substrate concentration on biohydrogen production from alfalfa by photosynthetic bacteria HAU-M1 [72]. The result showed that the highest hydrogen yield (55.81 mL/g) was attained at preliminary pH of 6.90, cellulase loading of 0.13 g/g, and substrate concentration of 31.23 g/mL. From the abovementioned studies on the effect of pH, it could be concluded that both hydrogen yield and hydrogen production rate are strongly depending on the initial pH, and the optimum pH is around 6.5 to 7. When the initial pH varied from 5 to 9, the hydrogen yield and hydrogen production rate increased quickly at first and reduced when pH was above 7. This might be explained by the fact that the inappropriate pH would constrain the bacterial growth and residence and, consequently, fewer hydrogen yield and slower hydrogen production rate.

On the other hand, Zhang and co-workers have investigated the relationship between mixing and lighting under different conditions and successfully obtained the optimum mixing speed and light intensity [65]. In this study, corncob and mixed bacteria strains HAU-M1 were utilized as feedstock and microorganism, correspondingly. The photo-fermentation was conducted by varying the combination of mixing speed and light intensity into high mixing speed (HM) with high light intensity (HL), low mixing speed (LM) with low light intensity (LL), LM with HL, LM with LL, and the dynamic mixing speed (DM) with dynamic light intensity (DL) and HM on diverse period. According to the investigational results and analysis, the entire photo-fermentation route consists of three phases, which are cell growth, hydrogen generation, and cell deterioration. It was found that the DM-DL showed the maximum hydrogen yield (84.7 mL/g TS) and regular hydrogen content, which accused that dynamic lighting and mixing would diminish the energy contribution and maximize the feedstock consumption. By considering that both mixing and lighting conditions could simultaneously realize a high efficacy biohydrogen production rate, especially under higher substrate concentration, more photo-fermentation biohydrogen production should be conducted under an optimized mixing and light intensity.

Theoretically, rheological properties define the behaviors of material under tensions causing by external forces, and every actual matter, whether a liquid, solid, or gas, straining upon exposure to external forces [82]. In biohydrogen production, the rheological behaviors of substrates expressively impact the energy consumption and hydrogen generation. Hereafter, the rheological behaviors of various concentrations of corn stover hydrolysate and its hydrogen formation capabilities were scrutinized under various intermittent stirring conditions [73]. It was perceived that this hydrolysate displayed pseudo-plastic flow and well fitted with the power-law model behavior at TS of 2.76–7.65%. For intermittent stirring, several conditions were employed: C1-static and stirring for 12 h, respectively; C2-static 16 h and stirring 8 h; C3-static 20 h and stirring 4 h; C4-static 22 h and stirring 2 h; and incessant stirring (C0) for control experiment, with stirring rate of 150 rpm, respectively. Among them, C2 achieved the maximum hydrogen yield of 57.63 ± 1.75 mL/g VS, 18.97% higher than static-culture. From this finding, it could be summarized that intermittent stirring could considerably enhance hydrogen yield with low-energy consumption and thus offered an economical approach for hydrogen production. By comparing with the previous study by Zhang and co-workers on the connection between mixing and lighting, it is believed that the maximum hydrogen yield of this study would be further enhanced upon optimizing the relationship between stirring rate and lighting conditions.

Even though a noteworthy number of brewery wastewater (BW) is produced throughout beer manufacture, its nutrients still tend to be recycled as a probable substrate to produce biohydrogen [74]. Hence, incorporation of PPME and BW as a mixed medium was explored expansively to study the effect of different substrate concentrations towards enhanced biohydrogen production performance. It was witnessed that biohydrogen yield was enriched by this combination, and the maximum biohydrogen yield (0.69 mol H_2/L medium) was acquired when the incorporation of 90% PPME + 10% BW (10B90P) is used. This is due to the improved light diffusion and nutrients into the incorporated medium by 10B90P, in which the best light efficacy is 1.97 %. It could be concluded that recycling and incorporation of two different effluents could promisingly improve the light penetration and nutrients through a medium, thus enhanced biohydrogen production. In another similar study, starch-rich agricultural wastes were used for photo-fermentation under different substrate concentration [83]. It was found that the different substrate concentrations could substantially influence the hydrogen production under the oscillation condition. Eight grams of substrate per 100 mL fermentation broth under oscillation has achieved the maximum hydrogen content of 38.36% and hydrogen yield of 510 mL/VS. This is because under shaking oscillation, the contact between the

photosynthetic bacteria and substrate will increase, thus preventing the deposition of the hydrogen-forming mixture for enhanced performance.

In other work, the effects of numerous pretreatment approaches, such as alkali, acid, hydrothermal, alkali-heat, and acid-heat on photo-fermentation, were inspected using corn straw [75]. It was perceived that all the abovementioned pretreatments efficiently demolished the structure of corn straw and enhanced its enzymatic saccharification. The highest hydrogen yield (137.76 mL/g TS) was gained upon pretreated with 2% NaOH. In contrast, the minimum cumulative hydrogen yield was attained when pretreated under alkali-heat (4% NaOH), with only 44.20 mL/g TS. This could be clarified that the concentration of the reducing sugar in the hydrolysate was a little high upon pretreated under alkali-heat and 4% NaOH and thus led to an enormous accumulation of by-products and low pH. Consequently, the hydrogen generation of photosynthetic microorganisms was inhibited. These results propose that a proper pretreatment of corn straw substrate could effectually abolish the structure of corn straw and improve the enzymatic saccharification, as well as biohydrogen formation performance.

Energy grass is an idyllic raw material of biomass energy that is usually composed of perennial arbor herbs or semi-shrubs. This material is rich in cellulose, hemicellulose, and lignin, with high calorific value and low ash content [84]. Before the biohydrogen production process, the crude fiber in the raw materials must be converted into small molecular organics via pretreatment and enzymolysis before being used by microorganisms. To investigate the viability of diverse energy grasses for hydrogen production from photosynthetic organisms, the enzymatic hydrolysis of energy grasses is a very essential procedure. Therefore, biohydrogen production from photo-fermentation by using energy grasses as substrates was investigated by changing enzymolysis time [76]. Ten energy kinds of grass were nominated in this study, which are *Arundo donax*, *Phragmites communis* (*Cav.*) *Trin. ex Steud.*, *Pennisetum alopecuroides* (L.) *Spreng.*, *Medicago sativa* L., *Miscanthus*, *Saccharum arundinaceum Retz.*, *Pennisetum purpureum Schum.*, *Panicum virgatum* L., *Pennisetum giganteum z.x.lin*, and *Triarrhena sacchariflora* (*Maxim.*) *Nakai*. It was perceived that *Medicago sativa* L. with enzymolysis time of 60 h achieved the highest hydrogen yield of 147.64 mL, while the *Arundo donax* with enzymolysis time of 36 h attains the maximum hydrogen production rate of 5.53 mL/(h g TS) and the maximum hydrogen production efficiency (1.15 mL/(h g TS)) was obtained using *Miscanthus* with enzymolysis time of 0 h. These results verified that there was a diverse optimum enzymatic hydrolysis time for different kinds of energy grasses for enhanced biohydrogen production

performance. To the best of our knowledge, the use of energy grass in photo-fermentation biohydrogen production is still scanty; thus, more research work is required to further explore the huge potential of various types of energy grass.

Recently, different fermentation modes including batch, continuous, and semi-continuous have been explored. Batch mode is functioned by consuming the initially given substrates and the reactions are depending on time [85]. In contrast, the continuous mode is time-independent due to simultaneous inflow and outflow occurred, while semi-continuous involves the removal and replacement part of fermentation medium by fresh medium. Inspired by that, the effect of the batch, semi-continuous, and continuous mode on biohydrogen production using dark fermentation effluents (DFEs) substrate and electron distribution was inspected [77]. It was observed that better hydrogen production was attained in the semi-continuous mode under 50% decanting volume ratio (DVR) and 24 h feeding interval time (FIT) conditions. The highest average hydrogen production rate (HPR) and hydrogen yields were 8.44 mL/h and 1386.22 ± 44.23 mL H_2/g TOC, respectively, and 37.71% substrate electrons separating to hydrogen were perceived in this mode. In semi-continuous mode, less bacterial are lost and the deficiency of trace elements could be avoided upon replacing fermented medium by fresh medium. For continuous mode, more substrate electrons were diverted toward soluble microbial products (SMPs) with the increasing of hydraulic retention time (HRT). This is due to the longer cell retention, the more chances for cell lysis to occur. SMPs frequently existed in fermentation broth due to cell lysis, which accounted for a certain amount of the substrate electrons. Hence, decreasing the SMPs production was an effective approach to increase hydrogen yield from the substrate by controlling fermentation mode and genetic and metabolic systems. From this work, it could be concluded that the semi-continuous mode is a promising commercial-scale operation due to its lower operational cost and high substrate conversion efficiency for enhanced hydrogen production.

Table 3 summarizes the details on various hydrogen production technologies including steam reforming [86], dry reforming [87], partial oxidation [88], auto-thermal reforming [89], water electrolysis, thermochemical water splitting [90], photocatalytic water splitting, dark fermentation, microbial electrolysis cell, bio-photolysis, and photo-fermentation. From the table, it can be observed that the non-hydrocarbon reforming technologies mostly operating at low pressure and temperature, as well as the use of a renewable source of feedstocks to produce hydrogen, which could reduce the hydrogen production cost. As one of the biological routes of hydrogen production, the photo-fermentation technique possesses a huge potential in terms of efficient hydrogen production, environmentally friendly approach, abundant raw material resources, and economically feasible.

Table 3 Comparison of difference hydrogen production technology

Technology	Reaction conditions	Feedstocks	Main products	Advantages	Disadvantages	References
Steam reforming	Endothermic, temperature (700–1000 °C), and pressure (3–25 bars)	Natural gas/CH_4	$CO + H_2$	Most effective industrial pathway for ~ 50% of the universal hydrogen production	Expensive noble metal catalysts and easily deactivated Ni-based catalysts	[86]
Dry reforming	Endothermic, temperature (650–700 °C)	CH_4 and CO_2	$CO + H_2$	Abundant feedstocks (biogas, coke-oven gas, etc.) and high temperature is beneficial to avoid carbon deposition	Rare and expensive noble metal catalysts and easily deactivated Ni-based catalysts	[87]
Partial oxidation	Exothermic, temperature (850–950 °C)	CH_4 and O_2	$CO + H_2$	Efficient and allows the use of smaller reactor for a much faster reaction	Poor stability in the presence of CO, H_2, and CH_4 gases, and require high temperature for high CH_4 conversion and syngas selectivity	[88]
Auto-thermal reforming	Mixed of endothermic and exothermic, temperature (950–1100 °C), pressure (100 bars)	CH_4	$CO_2 + H_2$	Improved reactor temperature control, reduced formation of hot spots, and avoided catalyst deactivation	High cost for low volume hydrogen production	[89]
Water electrolysis	Low temperature	H_2O	$H_2 + O_2$	Promising and sustainable method	Challenges of development efficient and durable catalysts	[10]
Thermochemical water splitting	High temperature (500–2000 °C)	H_2O	$H_2 + O_2$	Directly convert thermal energy into stored chemical energy as H_2	Requires extremely high temperatures	[90]
Photocatalytic water splitting	Low temperature and atmospheric pressure	H_2O	$H_2 + O_2$	Simple and environmentally friendly process	Limited visible light response, low charge carrier mobility, and high carrier recombination of the catalyst	[16]
Dark fermentation	Low temperature and atmospheric pressure	Carbohydrates, proteins, and glycerol	H_2, volatile fatty acids, and CO_2	Environmentally friendly, cost effective, no need for the existence of light energy, and continuous use of carbohydrate	Various toxic compounds can significantly limit sustainable method of hydrogen production	[1]
Microbial electrolysis cell	Low temperature and atmospheric pressure	Organic matter, including wastewater and other renewable resources	H_2	Mild operating conditions and high yield of H_2	Probability of the H_2 formed being effortlessly scavenged by methanogens, homoacetogens, and exoelectrogens and thus inhibited H_2 production	[37]
Bio-photolysis	Low temperature and atmospheric pressure	H_2O	$H_2 + O_2$	Eye-catching process that uses solar energy to change a readily available water to oxygen and hydrogen	Hydrogenase activity is highly sensitive to oxygen, thus inhibits the hydrogen production	[41]
Photo-fermentation	Low temperature. and atmospheric pressure	Sugars and volatile fatty acids	$H_2 + CO_2$	Broad raw material resources, utilize a wide range of light spectrums, and environmentally friendly	High nitrogen and ammonia content can suppress nitrogenase synthesis and dark color of the waste materials could reduce light penetration	[44]

4 Major challenges and prospects

The growing need for the reduction of carbon release has led to the increasing demand for hydrogen as an eye-catching alternative fuel. Nonetheless, the common hydrogen production technologies, including dry reforming, steam reforming, auto-thermal reforming, and partial oxidation, primarily involve the utilization of fossil fuel. This inevitably raises the demand for fossil fuels and also led to the emissions of greenhouse gases. By considering that, it is predicted that the use of alternative biohydrogen methods specifically a newly developed photo-fermentation will be comprehensively studied to meet the increasing demands of hydrogen. Besides, the enhancement of photo-fermentation for biohydrogen production has become a worldwide concern nowadays and numerous research works have been dedicated to achieving a high yield of hydrogen with low cost and low-energy consuming via this process. Even the photo-fermentation is greener and is capable to produce a high yield of hydrogen at mild reaction conditions; several enhancements are required to further improve the performance.

It is known that light is required to supply energy for electron transport and hydrogen generation in photo-fermentation. Nevertheless, due to the non-uniform light intensity spreading in the system, the entire photo-fermentation reaction site is commonly distributed into three parts, which are light growth zone, light inhibition zone, and light restraining zone [65]. Unfortunately, the three light zones could not provide a similar light utilization efficacy and energy consumption rate, and the worst fact is that one of those sections possesses inadequate light intensity to offer the essential energy for biohydrogen generation [91]. In this respect, the unceasing studies are required to improve the light intensity in the photoreactor for uniform energy distribution and enhanced hydrogen production. Besides, it is worth mentioning that the residue substrate and wastewater usually possess different shading capabilities that also could affect light penetration. For instance, the distinctive color aspects of wastewaters can be classified into three types: not too old wastewater is indicated by its light brown color; for wastewater that experiences decomposition or in storage for some time, the color is light or medium grey, while dark grey/black/brown representing septic wastewater has endured wide microbial decomposition [59]. The various colors of these wastewaters could strongly hinder the light penetration through the photobioreactor and form a shadowing effect on the bacteria and thus decrease the light conversion efficiency. This problem has limited the exploitation of wastewater and residues as a substrate for photo-fermentation hydrogen production. By considering these two factors related to light conversion efficiency, it is essential to apply an appropriate pretreatment procedure towards wastewater and residues substrates for enhanced light penetration, as well as to enlarge the light growth zone for improved light consumption rate and light conversion efficiency and consequently increase biohydrogen production.

As one of the potential lignocellulosic biomass resources, the forest residues account for about 50% of the entire forest biomass and could be exploited for biohydrogen production [92]. The forest residual waste contains wood chips, sawdust, wood bark, and the energy-producing ability of all these forest waste is roughly calculated to be 10,000 MW. The specific characteristics of forest biomass mostly comprise the existence of woody ash contents which make it stable and effortlessly controllable during transportation as compared with crop residues [93]. Besides, the abundant nature of forestry lignocellulosic biomass resources, being carbon neutral substrate, and the absence of any contestation with food supplies offer a chance to develop an environmentally clean and effective low-cost biohydrogen production technology [24]. For these reasons, the conversion of forest residues to bioenergy especially biohydrogen has seemed to be the main objective of the industries processing forest materials [94]. Up to now, however, to the author's best knowledge, there is no report on the exploitation of forestry biomass as feedstock for hydrogen production via the photo-fermentation process. In this respect, widespread research works have to be directed towards the utilization of forestry-based lignocellulosic biomass for efficient biohydrogen production via the photo-fermentation process.

Besides, it was previously reported that there are several inhibitory compounds usual present in wastewaters and food wastes such as furfural, ammonium, and polyphenols [59]. For instance, furfural is a hazardous toxic compound that could significantly prevent the hydrogen production, while the presence of ammonium ion at a higher level than its threshold value could harshly suppress the activity of the nitrogenase enzyme, which is the key hydrogen-producing enzyme of bacteria. Meanwhile, the polyphenol gave a darker color to the waste, thus reducing the efficiency of the pretreatment process involving the bacteria route. In this respect, a suitable approach is required to remove these inhibitory compounds during the pretreatment step before the photo-fermentation reaction. In the meantime, the pretreatments of the substrates in photo-fermentation usually involve the combination of different methods, such as physical-chemical and physical-biological methods, which are believed to be time- and energy-consuming processes. The search for uncomplicated substrates with a simpler pretreatment approach is urgently required to reduce the photo-fermentation cost.

The speedy growths in nanotechnology have broadened the opportunity of its applications in numerous fields such as food, pharmaceuticals, agriculture, and energy. The use of nanotechnology in these diverse industries is mostly ascribed to the novel characteristics of nanoparticles (NPs) which include their nanosize, structure, morphology, and reactivity. The role in harvesting energy has led to its application in

enhancing the hydrogen production by affecting biological activities of the living species and activate microbial metabolism at a very low concentration along with pH and thermal stability [95]. These sole criteria have led to the increasing choice of the NPs as promising materials for improved biofuel processes. In the biofuel industry, NPs are commonly employed as catalytic agents that act as electrons transporter, inhibitory compounds scavenger, and promoter for the activity of anaerobic consortia. Therefore, their applications for improved biohydrogen production are due to their impacts on the growth of microorganisms, the activity of metalloenzymes for hydrogen generation, and intracellular electron transport [96]. To date, the exploitation of nanoparticles as a supplement for enhanced biohydrogen production has progressively gained consideration and a few research works have verified its potential. In photo-fermentation, Fe is the most commonly used metal due to its potential as a stimulator which is related to the role of ferredoxin as an electron transporter in the nitrogenase enzyme system [97]. By considering that, more potential metal or metal oxide needs to be explored for further enhanced photo-fermentation hydrogen production. Besides, some alterations of the applications of NPs are still essential in the deliberations for further research, especially in terms of the sizes, type, and shapes of NPs in the scaling-up of photo-fermentation processes since most of the research only was performed under a controlled laboratory scale.

On the other hand, various strategies have been done so far to overcome the problems related to the photo-fermentation process including tailoring the light intensity and stirring condition, altering the pH, finding the best pretreatment of the substrates, as well as searching for the appropriate concentration of substrates and wastewaters. Nevertheless, as far as we know, the report on the exploration of efficient, environmentally friendly, and low-cost photobioreactor is still scanty. Chen and co-workers reported that conventional photobioreactors using external lighting systems suffer from several disadvantages [48]. For instance, the light intensity could easily decrease upon the shielding effects that occurred resulting from the rise of the cells and product concentration or biofilm coverage on the surface of reactor vessels. Additionally, the conservative light sources cannot be located too near with the bacterial culture due to its generation of heat even a tiny light path is supposedly preferable to attain excellent light effectiveness. Because of that factor, a drastic approach and a prolonged innovation have to be performed to allow this lab-scale photobioreactor to become a future plant-scale technology for biological hydrogen production.

5 Conclusion

In summary, this article reviewed some advantages of uses of hydrogen as a green alternative fuel to substitute conventional fossil fuel. Numerous hydrogen production techniques were

deliberately included and compared with the more environmentally friendly technology of biohydrogen production. Some biohydrogen production methods were thoroughly explained to emphasize the beneficial use of the selected biohydrogen routes. The inclusive criteria and common photo-fermentation biohydrogen production mechanism were presented to highlight the benefits of this method than other techniques. Furthermore, various lignocellulosic biomasses that could be potentially used as feedstocks for photo-fermentation biohydrogen production have been mentioned together with the suitable pretreatment procedure before their use in photo-fermentation. The crucial section in this review involving the screened factors impacting the photo-fermentation biohydrogen production process for enhanced performance was particularized comprehensively. Finally, the major challenge and prospects are also comprised to expose the unexplored characteristics of a promising, efficient, and greener biohydrogen production via photo-fermentation. It is anticipated that all the aforementioned information may deliver valuable acumen into the fabrication of efficient photo-fermentation of lignocellulosic biomass for biohydrogen production.

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