Biomass Conversion and Biorefinery
https://doi.org/10.1007/s13399-020-01161-7

REVIEW ARTICLE

Lignocellulose-derived monosugars: a review of biomass pre-treating techniques and post-methods to produce sustainable biohydrogen

Pham Thi Phan[1] · Ba-Son Nguyen[2] · Trong-Anh Nguyen[1] · Ashok Kumar[3] · Van-Huy Nguyen[4]

Received: 3 August 2020 / Revised: 9 October 2020 / Accepted: 18 November 2020

Abstract

Biohydrogen (H_2) is considered as a prospective energy source for altering of exhausting fossil fuel-based hydrogen in the coming years. Among biomaterials, lignocellulose is the most abundant renewable feedstock for the second generation biohydrogen production through many processes. The conventional microbial fermentation and the photocatalytic reforming have received considerable attention that could convert the monosugars (mainly glucose and xylose) of the lignocellulosic materials into biohydrogen. In general, to obtain these monosugars, the lignocellulosic materials must be pre-treated through various complicated processes. This review focuses on various integrated pre-treating lignocellulosic material techniques and their advantages and disadvantages, including pretreatment, hydrolysis, and detoxification methods to get monosugars. Additionally, the state-of-the-art accomplishments in the post-methods, including microbial fermentation (including photo-fermentation and dark fermentation), microbial electrolysis, and photocatalytic reforming, for further converting monosugars into sustainable biohydrogen, are favorably highlighted. Finally, the perspectives for material pre-treating techniques and future challenges for post-methods to enhance biohydrogen are also discussed and intensified.

Keywords Lignocellulose · Biohydrogen production · Pretreatment · Hydrolysis · Detoxification

Abbreviations

AAS	Aqueous ammonia soaking
AFEX	Ammonia fiber explosion
$^{NCN}CN_x$	Cyanamide-functionalized carbon nitride
CO_2	Carbon dioxide
CS	Cassava stem
CB	Conduction band
(e^-)	electron
(h^+)	hole
(•OH)	Hydroxyl radicals
H_2	Hydrogen/ Biohydrogen
HMF	Hydroxymethyl furfural
PIL	Protic ionic liquid
VB	Valence band

✉ Van-Huy Nguyen
nguyenvanhuy20@duytan.com.vn

[1] Department of Chemical and Environmental Engineering, Lac Hong University, Bien Hoa, Dong Nai 810000, Vietnam

[2] Key Laboratory of Advanced Materials for Energy and Environmental Applications, Lac Hong University, Bien Hoa, Dong Nai 810000, Vietnam

[3] Department of Biotechnology and Bioinformatics, Jaypee University of Information Technology, Waknaghat, Solan, Himachal Pradesh 173 234, India

[4] Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam

1 Introduction

Hydrogen (H_2) is a perspective of future fuel as it has high heating value and used in many sectors. Besides, the alternation of fossil fuel–based gasoline and diesel by hydrogen can contribute to efforts to reducing carbon dioxide (CO_2) emission and environmental pollution from the combusting of these products because when hydrogen is combusted, it produces water as a clean main product [1–3]. Therefore, hydrogen fuel demand is more and more increasing. Currently, the synthesis gas derived from hydrocarbon fossil fuel and water is the primary source of hydrogen. Since this conventional approach is based on fossil fuel, it faces difficulties due to fossil fuel depletion [4, 5]. With approximately a 1.1% increase per year, fossil fuel is running out soon [3]. To tackle the above issue, looking for another hydrogen source is a necessary and attractive goal.

Published online: 25 November 2020

As a sustainable hydrogen source, recently, biohydrogen has got great attention because it can be produced from various biomass sources through biological route (dark fermentation and photo-fermentation) or thermochemical route (gasification or pyrolysis) [6–9]. Biohydrogen can be produced from non-waste feedstocks such as sugar-containing crops (including glucose, xylose, and sucrose in starch), known as the first-generation biohydrogen [10–12]. However, using these sugars from starch for first-generation biohydrogen production faces food security [13, 14]. Therefore, in point of material source and environmental view, biohydrogen produced from biomass waste, which also contains a significant amount of glucose and xylose such as lignocellulosic waste, is an ideal renewable energy. Unlike the first-generation biohydrogen, biohydrogen production from biomass waste, known as the second-generation biohydrogen, is a promising sustainable energy source. In this route, the lignocellulosic waste from crops, planting, etc., which is renewable, cheap, and abundant, is used as feedstocks. Additionally, lignocellulosic waste conversion to biohydrogen and biofuel could effectively reduce CO_2 emissions from burning lignocellulosic crop residues on open field [15–17]. Thus, biohydrogen production from lignocellulose materials is an appreciated and prospective goal.

There are many methods and processes to produce biohydrogen. However, two recent concerned approaches to produce second-generation biohydrogen from monosugars such as glucose and xylose are (1) using microorganisms via fermentation and (2) via photocatalytic reforming. On the one hand, the productions of biohydrogen through fermentation include the dark fermentation and photo-fermentation. In this route, microorganism plays an essential role in converting glucose and xylose to hydrogen via metabolism [18–24]. On the other hand, the biohydrogen generation, which is based on the photocatalytic reforming route, is promoted by photocatalysts with a light source [25–29]. The first or the second routes to produce second-generation biohydrogen from lignocellulose-derived sugars, glucose, and xylose are essential materials for processes. Therefore, material treating techniques to obtain glucose and xylose are the key for succeeding in biohydrogen production from lignocellulose material.

To date, there were only a few reviews for the production of hydrogen from lignocellulose. For example, Singh et al. focused on producing hydrogen from untreated/treated lignocellulose [30]. On the other hand, Kucharska et al. and Bajpai studied the general lignocellulosic treating to produce hydrogen and other biofuels by biochemical processes [30, 31]. This review highlights pre-treating techniques (pretreatment, hydrolysis, detoxification) for lignocellulose to obtain the monosugars (mainly glucose and xylose). The monosugars, which are considered raw material sources, are continually used to produce biohydrogen (via the next step of fermentation or photocatalytic reforming). Finally, the perspectives for material treating techniques and future challenges to enhance biohydrogen are also discussed and highlighted.

2 Techniques for material pre-treating toward production of biohydrogen

2.1 Lignocellulose structure

Lignocellulose is a complex structure composed mainly of cellulose, hemicellulose, and lignin, as illustrated in Fig. 1. Typically, the celluloses are long glucan polymers of linear chains of hundreds to many thousands of 1,4-beta bonded anhydroglucose units [32]. Hemicelluloses are polysaccharides composed of shorter chains of linear or branched units. They are intertwined with a linear chain structure of cellulose. Lignin molecules are closely bound to cellulose and hemicelluloses and surround them, thereby protecting the cellulose-hemicellulose matrix, making the structure difficult to break [33–35].

The percentages of cellulose, hemicelluloses, and lignin in lignocellulosic materials vary depending on their source. The components of some lignocellulosic materials are shown in Table 1 [36, 37, 39, 46]. Some lignocellulosic materials have very high cellulose and hemicellulose contents, e.g., sugar cane bagasse, cassava stem, rice straw, and wheat straw. They are among the most commonly explored sugar supply sources for second-generation biohydrogen production.

2.1.1 Cellulose

Cellulose is an essential structural component of the cell wall of plants. The general formula of cellulose is $(C_6H_{10}O_5)_n$. It is a long glucan polymer consisting of linear chains of hundreds to many thousands of 1,4-β bonded anhydroglucose units. The bonds between sugars are created when water is eliminated by combining the −OH group (Fig. 1). The link between two sugars produces a disaccharide called cellobiose. Cellulose includes crystalline and amorphous regions. The significant proportion is crystalline cellulose [35, 48–50].

2.1.2 Hemicellulose

Hemicelluloses are matrices of polysaccharides, which are composed of shorter chains of 500–3000 sugar units. Unlike cellulose, a linear polymer, hemicelluloses are linear or branched. They contain various sugars, including pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, mannose, and galactose), and some other compounds, as illustrated in Fig. 2. Hemicellulose has a random, amorphous structure with little strength. Therefore, it is easier to break it than

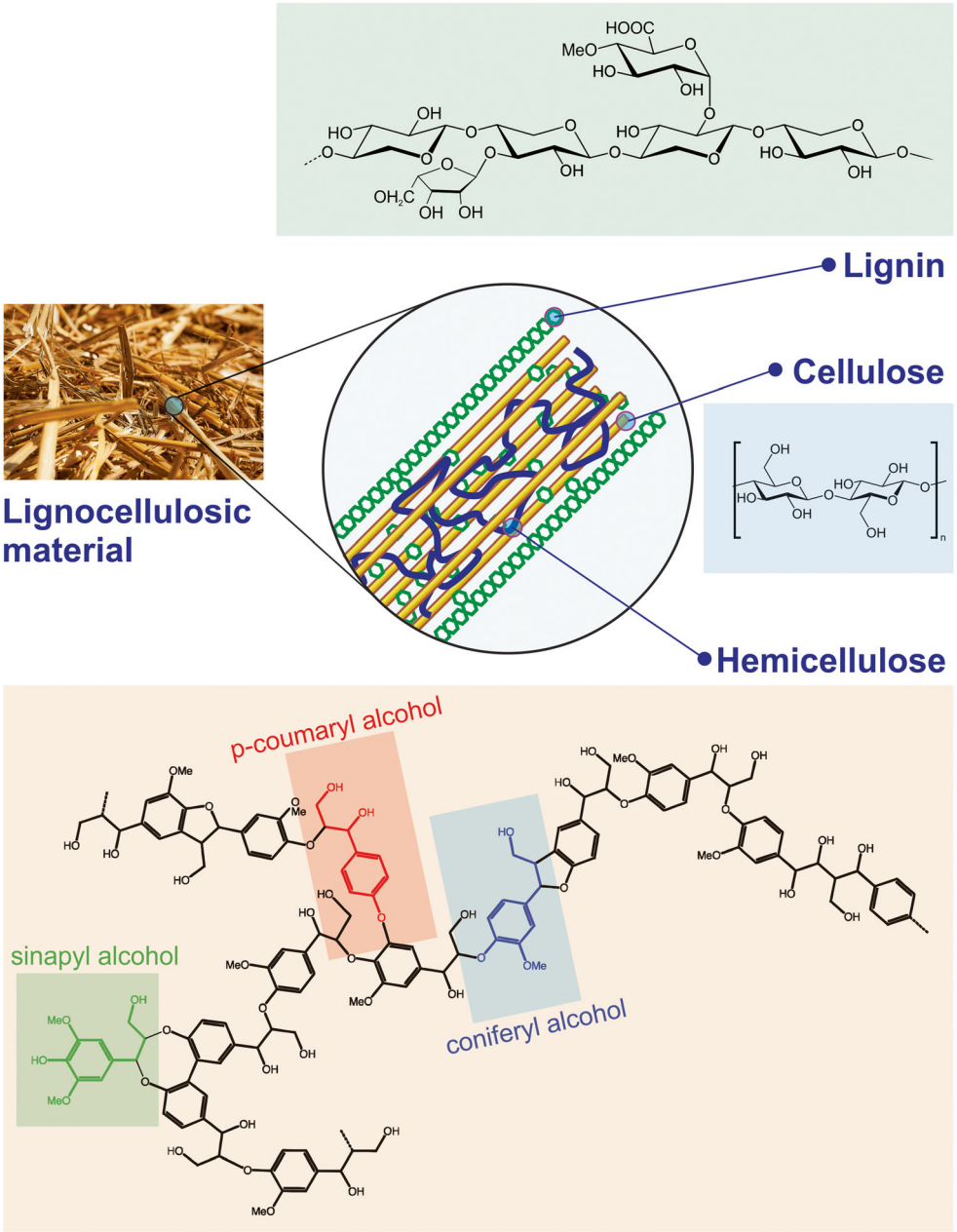

Fig. 1 Structure of cellulose, hemicelluloses, and lignin in lignocellulosic materials. Adapted from Jensen et al. [32]

Table 1 The components of some lignocellulosic materials (as percent dry weight)

Raw material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref.
Corn cobs	42–45	35–39	14–15	[36, 37]
Sugar cane bagasse	42–48	19–25	20–45	[36, 38]
Wheat straw	29–45	20–32	8–21	[36, 37, 39]
Rice straw	28–47	19–28	5–24	[36, 37, 39]
Corn stalks	39–48	21.3–43	7.3–16	[37, 40, 41]
Corn stover	37	31	13–26	[42, 43]
Bagasse	45–55	20–25	18–24	[44]
Poplar	44.5	22.5	19.5	[45]
Barley straw	31–45	27–38	14–19	[37]
Cassava stem	29.8–42.1	11.6–29.8	19.1	[46, 47]

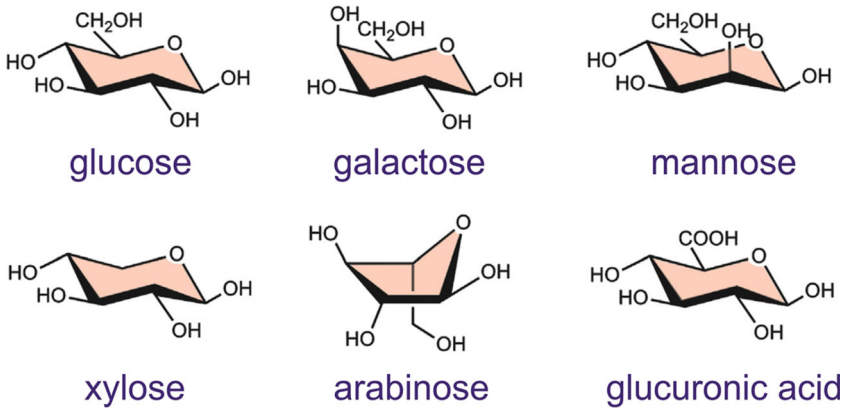

Fig. 2 The structures of various types of hemicelluloses. Reprinted with permission from Li et al. [51]; license no.: 4921471096924

cellulose because the lengths of hemicellulose chains are short, and these polymers do not aggregate, even when they co-crystallized with cellulose chains [35, 48–50].

The hemicellulose chains' backbone can be a mixture of different sugars (heteropolymer) or a single sugar repeated unit (homopolymer). Depending on the main sugar in the backbone, hemicellulose can be xylan (if xylose is the main sugar), mannan (if mannose is the main sugar), etc. [35, 48, 50].

Because of such a structure, the hemicellulosic structure is broken and dissolved more quickly than cellulose. It is challenging to retain monosugars in the hemicellulosic fraction in the solid phase to become feedstock for the next step and then for hydrogen production. It notes that pentoses are often lost in pre-treating lignocelluloses. Therefore, hemicellulosic composition in lignocellulosic material has not received considerable attention in the second biohydrogen production. However, the analysis of lignocellulosic materials (Table 1) shows that hemicellulose fraction from lignocellulose should be considered because the hemicellulose fraction is also significant and many sugars, especially xylose, can be a substrate for hydrogen production. If this fraction can be retained in hydrolysate and becomes the substrate for production, biohydrogen concentration would significantly improve.

2.1.3 Lignin

Lignin is a complex three-dimensional structure which is composed of phenyl propane units. It is a large molecule having more than 10,000 units, and it is a relatively hydrophobic and aromatic polymer. It is closely bound to protect cellulose and hemicelluloses (Fig. 1). Therefore, in biohydrogen production from lignocellulosic materials, lignin structure must be broken to release cellulose and hemicelluloses, and facilitate hydrolysis. Besides, in biohydrogen production, lignin and its derivate are considered waste and toxicants for microbial growth. Therefore, lignin should be removed before performing hydrolysis to enrich sugar concentration and/or lignin derivate should be removed before fermenting if bioconversion is employed to generate hydrogen from lignocellulose hydrolysate.

2.2 Lignocellulosic pre-treating techniques

In biohydrogen production from the lignocellulosic-derived monosugars (glucose and xylose), the material must undergo the main steps, as mentioned earlier, because of the lignocellulose structure mentioned earlier Fig. 3. After being ground, lignocellulose is often passed directly/indirectly through various pre-treating steps to produce monosugars. Typically, the first step is pretreatment, which breaks down lignin structure

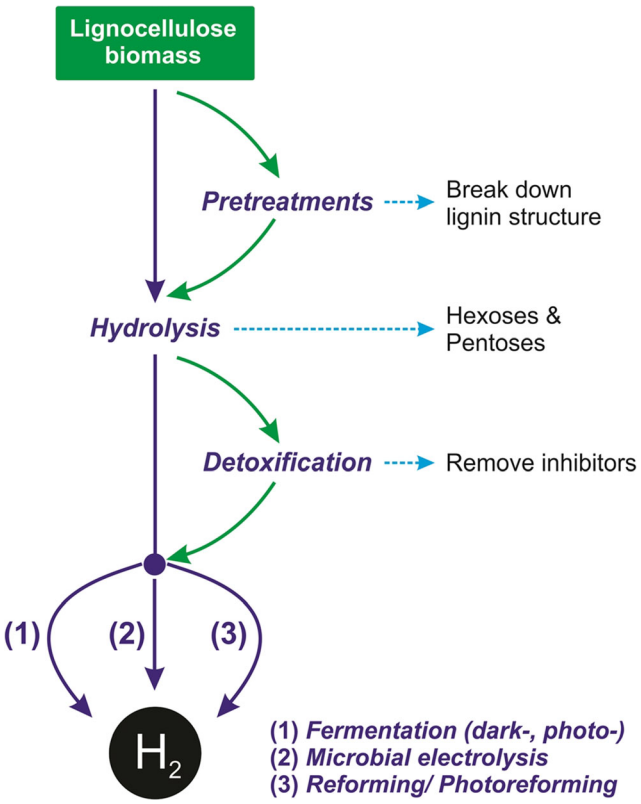

Fig. 3 The outline of biohydrogen production from lignocellulosic-derived monosugars

to improve or facilitate hydrolysis of cellulose and hemicellulose [52, 53]. The next is hydrolysis, which is splitting cellulosic and hemicellulosic polymers to release hexoses and pentoses for fermentation [54, 55]. After that, detoxification may be applied to remove inhibitors that are formed during hydrolysis. If the hydrolysis is enzymatic, detoxification is not necessary because this hydrolysis method does not release many inhibitors [56–59]. The last step is producing biohydrogen from glucose and xylose through microbial fermentation or photocatalytic reforming processes, as illustrated in Fig. 3.

2.2.1 Pretreatment techniques

Pretreatment of lignocellulosic biomass is the first step before being used as a feedstock for biohydrogen production [60]. It aims to break the lignin matrix to release cellulose and hemicellulose fragments to facilitate the succeeding hydrolysis process [52, 53, 61]. Most of the lignin contents dissolve in the liquid phase and are separated from the cellulose and hemicellulose. Lignin is one of the value-added products beside sugars; the lignin recovery and use should be concerned to increase the value of lignocellulose [61, 62]. A number of different pretreatment methods are collected and shown in Table 2. Based on the reaction's nature, the pretreatment could be categorized into three primary classes, including biological [52, 63–65], physical [52, 63–66], and chemical [52, 63–67] processes.

Biological pretreatment techniques use microorganisms to destroy the lignin matrix. The microbes are often fungi such as brown-, white-, and soft-rot fungi because they often have lignin-degrading enzymes such as peroxidases and laccase. These enzymes can break the lignin structure at neutral pH and in both aerobic and anaerobic conditions. It is a cheap and environment-friendly method. However, its delignification efficiency is lower than other methods, and it also requires longer treatment time [31, 68–70]. A study conducted by Su et al. showed that three lignin-degrade enzymes were secreted simultaneously by *Myrothecium verrucaria* during the biopretreatment process. After 96 h, at 29 °C, 42.3% of lignin in corn stover was removed by these fungi [70].

Hydrothermal physical pretreatment techniques include irradiation and steam explosion, among others. They do not have so much effect as breaking the lignin structure, but they make the material swell, thereby facilitating the next treatment step [52, 53]. Therefore, this method is preferred to accompany mild chemical reagents to obtain a high yield of reducing sugars.

Chemical pretreatment techniques often use chemical reagents such as an acid (e.g., carbonic, hydrochloric, hydrofluoric, nitric and phosphoric, sulfuric), alkali (e.g., calcium, sodium, and ammonia hydroxide), and solvents among others. These method's advantages are its high efficiency and shorter treatment time requirement [31, 71, 72]. Among them, alkaline pretreatment has been most often explored because it is relatively cheaper than other methods. However, if enzymatic hydrolysis follows an alkali pretreatment, large amounts of acid will be needed to adjust the mixture's pH to ca. 5. If acid hydrolysis will be applied, acid pretreatment will be more suitable. Also, as mentioned earlier, hemicellulose structure is easily broken through chemical pretreatment, and pentoses are dissolved in the pretreatment liquid phase. If, after chemical delignification, the material is washed to remove lignin, a significant amount of pentoses is also lost. Once pentose (mainly xylose) is lost, hydrogen production from lignocellulose-derived glucose and xylose could not achieve high efficiency. Size reduction, such as chopping and milling, and chemical methods are applied for a more effective pretreatment of lignocellulosic materials [46, 53, 59].

An alkaline pretreatment study was conducted to evaluate deligninfication by Kim and Lee [73]. In this study, aqueous ammonia soaking (AAS) was applied. AAS is a chemical pretreatment method using aqueous ammonia like reagent to break the lignin structure surrounding cellulose and hemicellulose efficiently. Because this method does not operate at high temperature and ammonia is not a potent reagent like other chemical pretreatment methods, AAS can remain significant hemicellulose fraction in the solid. Kim and Lee's experiment on corn stover showed that this method removed 62% of lignin but retained 100% glucan and 85% of xylan after 12 h [73]. In Yadav et al.'s report, 0.2 M potassium (KOH) was employed to remove lignin in rice straw for 4 h at room temperature (around 30 °C). The result was nearly 80% lignin elimination and 2% sugar loss [74]. Besides the mentioned studies, there are many other pretreatment pieces of research on lignocellulosic materials. A summary of some of them is collected in Table 3.

2.2.2 Hydrolysis techniques

Hydrolysis is an essential step in biohydrogen production from lignocellulosic-derived glucose and xylose [80, 81]. Through the hydrolysis process, for which there are various methods, namely, chemical, biological, and physical methods, cellulose and hemicelluloses release hexoses (mainly glucose) and pentose (mainly xylose) for further biohydrogen production. Typically, physical methods (temperature, pressure) are combined with biological or chemical methods. Either enzymes or chemical reagents are used as catalysts. Examples of the latter are acids (e.g., sulfuric acid, hydrochloric acid) and alkali (e.g., sodium hydroxide) [59, 82, 83]. The advantages and disadvantages of these methods are presented in Table 4.

As presented in Table 4, it is favorable to use chemical methods for hydrolysis. The enzymatic hydrolysis method is environment friendly but still expensive because of the high cost of enzymes. Although chemical methods will

Table 2 The general principles, advantages, and disadvantages of various pretreatment techniques

Pretreatment	Factors	Effect	Advantages	Disadvantages	Ref.
Biological	Microbe (fungi, at neutral pH and in both aerobic and anaerobic condition) or enzyme	Remove lignin	• Low energy consumption. • No equipment corrosion problems • Do not produce inhibitors	• Long time; • Low efficiency	[52, 63–65]
Physical	Irradiation (electron beam, gamma-ray, microwave) Electric (pulsed electrical field)	Soften lignin and lignocellulose structure	• Do not produce inhibitors • Simple process	• Only soften lignin and lignocellulose structure, still not break structure to remove lignin	[52, 63, 65]
	Hydrothermolysis (liquid hot water)				[52, 63, 66]
	Steam explosion (high pressure steam)				[52, 63–66]
Chemical	Alkaline extraction (calcium, sodium and ammonia hydroxide)	Decrease cellulose crystallinity; Partial or complete hydrolysis of hemicelluloses; Delignification	• Requires short reaction time; • High conversion of hemicelluloses	• Corrosive	[52, 63, 65–67]
	Acid hydrolysis (carbonic, hydrochloric, hydrofluoric, nitric, phosphoric, sulfuric)		• Requires long reaction time at low temperatures and low pressures.	• Part of irrecoverable salt formed. • Corrosive.	[52, 63–67]
	Ammonia fiber explosion (AFEX)		• Requires short reaction time • Not corrosive for equipment • Do not produce inhibitors • Allows recovery of lignin and ammonia	• Not effective with high lignin biomass; • Requires high pressure	[52, 63–65]
	Oxidant (ozone, wet oxidation)		• Highly effective • Requires short reaction time • Do not produce inhibitors	• Expensive; • Good only for low lignin content.	[52, 64]
	Organic solvent (ethanol–water, benzene–water, ethylene glycol, butanol–water)		• High delignification efficiency • Allows solvent reuse • Require short reaction time • Do not produce inhibitors	• Some solvents are explosive and flammable	[52, 63–65]
	Protic ionic liquid (PIL)	Simple extraction of lignin from lignocellulosic biomass	• High delignification efficiency; • Recovers lignin and recycled PIL; • Requires short reaction time • Do not produce inhibitors	• Complicated process	[52, 63, 64, 66, 67]

Table 3 A summary of some pretreatment researches on lignocellulosic materials

Pretreatment	Lignocellulose	Experimental conditions	Lignin removal (%)	Sugar retaining (%)	Ref.
Biological	Corn stover	*Myrothecium verrucaria*; 4 days; 29 °C	42.3%	-	[70]
	Radiata pine	*Trametes versicolor*; 5 weeks; 25 °C	22%	77%	[75]
	Bamboo culms	*Punctularia sp.* TUFC20056; 12 weeks; 21 °C	> 50%	-	[76]
Chemical	Corn stover	NH_3 15%;12 h; 60 °C; 1:6 *w/v*	62%	100% glucan and 85% of xylan	[73]
	Rice straw	KOH 0.2 M; 4 h; 30 °C; 1:10 w/v	80%	98%	[74]
	Corn stalk	NaOH 5%; 24 h; 60 °C; 1:20 w/v	71.8%	79.6%	[77]
	Corn stalk	H_2SO_4 5%; 24 h; 60 °C; 1:20 w/v	64.3%	71.6%	[77]
	Sugarcane bagasse	NaOH 1%; 0.5 h; 121 °C; 1:10 w/v	62.3%	-	[78]
	Polar	NaOH 0.4 M; 170 °C; 7 min (combined microwaves)	61.9%	-	[79]
	Elephant grass	NaOH 3%; 1 h; 121 °C; 1:10 w/v	81.0%	72.3% glucan Xylan: no data	[62]

require corrosion-resistant reaction vessels, they give higher sugar yields at shorter reaction times. Hydrolysis methods involving enzyme, dilute, or concentrated chemical reagents, e.g., NaOH, HCl, etc., were employed by Nuwamanya et al. to derive sugar from non-food parts of cassava (untreated) [83]. They reported 47% sugar recovery in non-food parts of cassava (untreated) through the enzymatic method and 56% through either NaOH or HCl hydrolysis. Acid hydrolysis has an advantage over alkali hydrolysis in terms of reducing xylose yield from hemicellulose. There are significant amounts of xylose in lignocellulosic materials; as earlier discussed, if these fermentable sugars are released, biohydrogen yield will be increased, and biohydrogen production from lignocellulose will be more economical. The two-stage sulfuric acid hydrolysis method has been applied in several studies to get a high yield of lignocellulosic-derived sugars [59, 84]. In a study of cassava stem (CS) hydrolysis, at 20 g CS L^{-1}, complete hydrolysis (glucan 96%, xylan 85%) was achieved; at higher CS dosage (100 g CS·L^{-1} and 200 g CS·L^{-1}), the hydrolysis of glucan and xylan was slightly reduced at 76–78% and 75–91%, respectively [59]. However, in biohydrogen production via photocatalytic reforming, a mildly basic condition is favorable for biohydrogen reforming because the photocatalytic reaction is better in a little high pH [11, 27, 28]. It is a convenience in pH adjustment if alkali hydrolysis is applied.

Table 5 shows the results of some lignocellulosic hydrolysis. Although significant efforts have been made for hydrolysis of lignocellulosic-derived glucose and xylose, a mechanistic and kinetic understanding of the process is required to implement this technology at large scale further.

2.2.3 Detoxifying hydrolysate techniques

Because of its high efficiency, chemical hydrolysis has been used to saccharify various lignocellulosic materials [59, 82, 83, 86]. However, this method, hydrolysate staying in an acidic or basic environment and at high temperatures and pressures, also leads to the formation of substances that inhibit the succeeding biohydrogen forming via biotechnological process [87, 88].

The generation of inhibitors from the hydrolysis of lignocellulosic material is illustrated in Fig. 4 [87, 88]. The purpose of hydrolysis is to break cellulose and hemicellulose chains to release sugar units. However, sugars and lignin components are also degraded to inhibitors for fermentation microorganisms. Six carbon sugars (glucose from cellulose, mannose, and galactose from hemicellulose) may be converted to hydroxymethyl furfural (HMF). Five carbon sugars (xylose and arabinose from hemicellulose) may be converted to furfural. Moreover, phenolic compounds may form from lignin

Table 4 Advantages and disadvantages of various methods for hydrolysis of lignocellulosic materials

Hydrolysis methods	Advantages	Disadvantages	Ref.
Chemical	• Higher sugar yield • Short time	• Corrosive • Requires neutralization for the next step • Produce inhibitors	[46, 50, 52, 82, 83]
Biological/enzymes	• Not corrosive • Do not produce inhibitors	• Requires long reaction time; • Low sugar yield • Expensive	[50, 52, 82, 83]

Table 5 Result of some lignocellulosic hydrolysis studies

Hydrolysis	Lignocellulose	Experimental conditions	Reducing sugar (%)	Ref.
Biological	Poplar	Enzymes; 42 °C; 24 h	> 71%	[79]
	Oat straw (acid-alkali pretreatment	Enzymes; 50 °C; 3 days	86.3%	[85]
	Non-food parts of cassava (untreated)	Enzymes; 5 days	47%	[83]
Chemical	Non-food parts of cassava (untreated)	NaOH 1 M; ratio 1:1 w/v; 5 days	56%	[83]
	Non-food parts of cassava (untreated)	HCl 1 M; ratio 1:1 w/v; 5 days	56%	[83]
	Cassava stem	Two stage sulfuric acid, 1 h, 111 °C	> 75%	[59]

components and may also be among microorganisms' inhibitors [46, 87, 88]. The effect of inhibitors on chemical hydrolysates in hydrogen production via photocatalytic reforming routes seems not mentioned. However, the impurity of hydrolysates and color from inhibitors has certainly hindered biohydrogen production via these routes. Compared to the photocatalytic reforming route, the effect of inhibitors in chemical hydrolysates on hydrogen production and biofuels via fermentation has been confirmed in many studies [46, 59, 87]. Hence, detoxification is an essential step in hydrogen production from chemical hydrolysates of lignocellulose. In many studies, inhibitors are removed via overlying and adsorption by activated carbon or charcoal. However, sugars are also lost in this process [59, 74, 89]. The efficiency of furfural removal by overlying and activated charcoal was evaluated by Tanaka et al. on cassava stem acid hydrolysate [59]. All furfural was eliminated in this study, but there was a declination of glucose from 63.2 to 46.0 g L^{-1}. Yadav et al. was conformed that the furans and phenols in rice straw acid hydrolysate were detoxified by overlying and activated charcoal [74]. Furans was reduced from 0.2 to 0.025 mg L^{-1} (88.4% removal) and phenolics was decreased from 0.95 to 0.14 g L^{-1} (84.6% removal). The sugar was also lost from 31 to 30 g L^{-1} (3%). Thus, costs and efficiency must be considered to apply or not detoxification steps to prepare glucose and xylose for biohydrogen production.

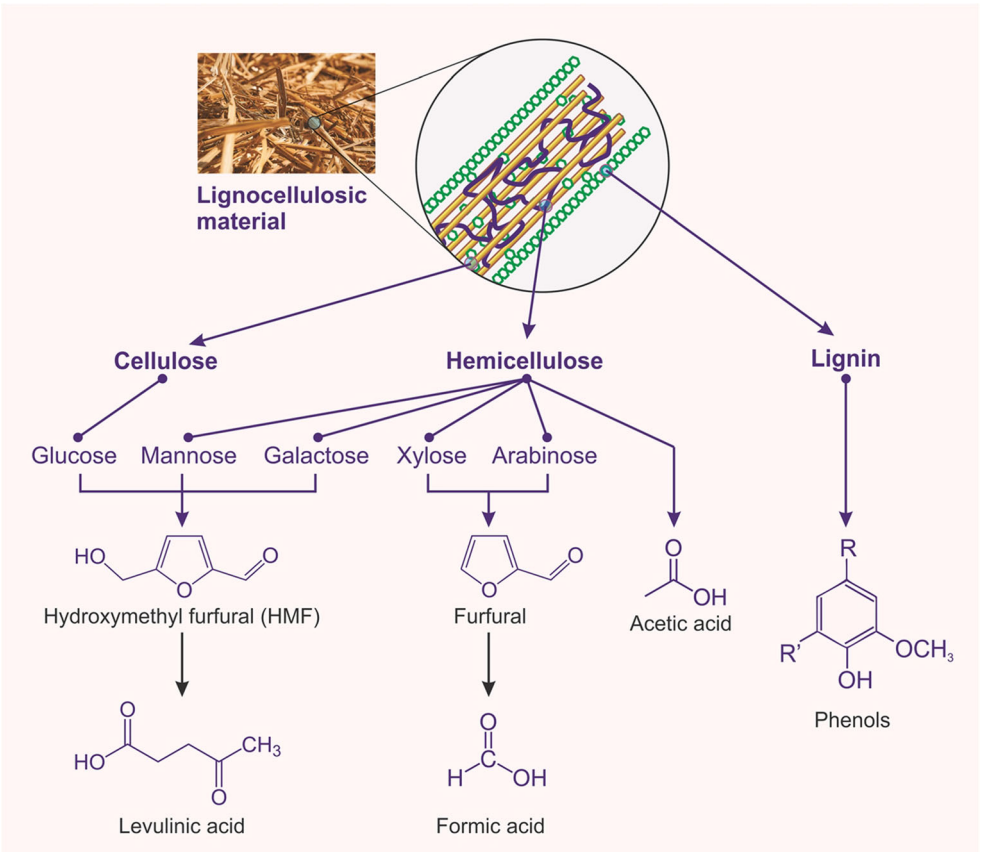

Fig. 4 The generation of inhibitors from chemical hydrolysis of lignocellulosic material

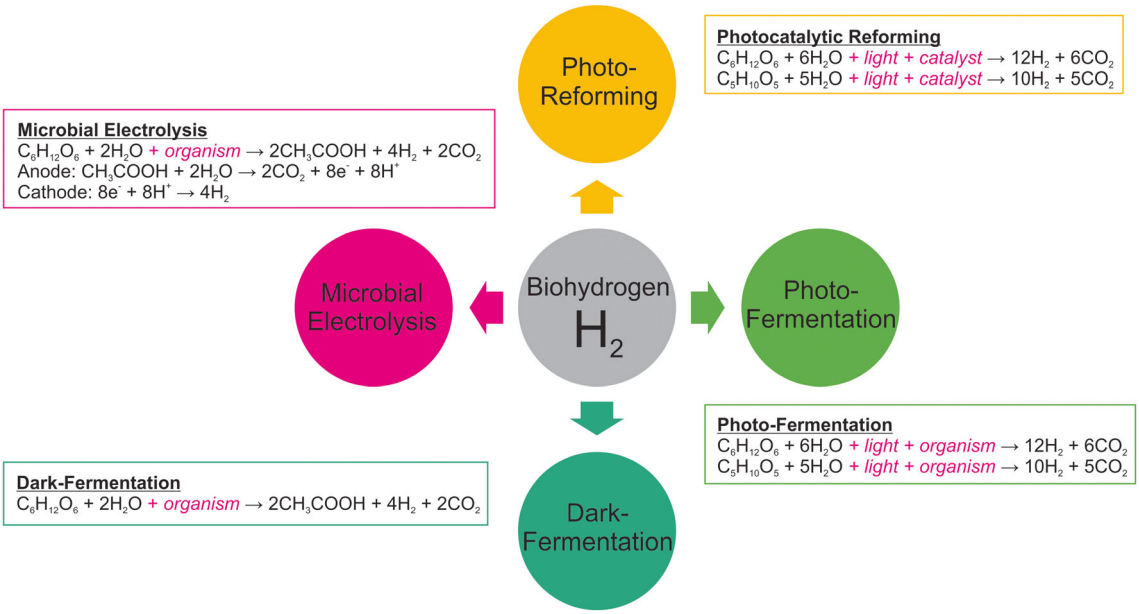

Fig. 5 The possible chemical reactions to generate biohydrogen (H_2) by conversion engineering of monosugars (glucose and xylose)

3 Current status of post-methods to produce biohydrogen from lignocellulose-derived monosugars

As a globally sustainable resource, the lignocellulosic-derived sugars have been proposed as an alternative feedstock to produce biohydrogen. To promote this perspective approach, material treating technology is a crucial matter [90]. Depending on conversion engineering of monosugars (glucose and xylose) to hydrogen (e.g., fermentation, microbial electrolysis, or photocatalytic reforming), a suitable hydrolysis method (accompany with or without appropriate pretreatment and detoxification steps) should be considered. Overall chemical reactions involved in production of biohydrogen, including the photo-fermentation, dark fermentation, microbial electrolysis, and photo-reforming, are compiled in Fig. 5.

To date, monosugars, such as glucose and xylose, have been pursued in many studies and achieved specific results. The details of some recent researches on post-methods to produce biohydrogen from lignocellulose-derived glucose and xylose are summarized in Table 6.

In summary, as considering hydrogen production via the fermentation route, the maximum theoretical hydrogen concentration per sugar is 12 mol mol^{-1} (66.6 mmol·g^{-1}) for glucose and 10 mol mol^{-1} (62.4 mmol g^{-1}) for xylose. In another approach, microbial electrolysis is promoted by the reduction of protons to generate hydrogen, called bioelectrohydrogenesis [101, 102]. This concept could effectively utilize the wastewater and agro-industrial residues that contain biopolymers (e.g., cellulose and starch) to produce biohydrogen [97]. The most challenging of this process is maintaining the stability of the electrical potential at both the bioanode and biocathode chambers [103, 104]. Recently, the light-driven conversion of lignocellulose has received considerable attention. In a previous study, Huang et al. proposed the general scheme of a photocatalytic system that combines biomass oxidation and water splitting, as seen in Fig. 6a [105]. First, the reaction is theoretically initiated by the excitation of the photocatalytic semiconductors under the light irradiation condition (the light energy (hν) ≥ the bandgap energy (E_{bg}) of photocatalysts). Then, an electron (e^-), which drops a hole (h^+), is pushed from the valence band (VB) to the conduction band (CB) of photocatalyst, which leads to generation of (e^-)-(h^+) pairs. Therefore, the presence of lignocellulose-derived substances as electron donors (sacrificial reagents or hole scavengers, denoted here as $C_xH_yO_z$) could react irreversibly with (h^+) to produce CO_2 and H_2O. This chemical reaction occurs either directly or indirectly via the forming of hydroxyl radicals (•OH). The remaining (e^-) simultaneously reduce protons (H^+) to generate H_2 molecules, followed by the H_2 evolution. In typical, Kasap et al. reported a cyanamide-functionalized carbon nitride, $^{NCN}CN_x$, for the biomass photo-reforming [99]. The possible mechanism of H_2 generation via the photo-reforming of lignocellulose over $^{NCN}CN_x$ and H_2 production cocatalysts is illustrated in Fig. 6b. The H_2 yield could reach to 202 μmol gCN_x^{-1} h^{-1}. This idea offers new

Table 6 Recent studies on biohydrogen production from lignocellulose-derived glucose and xylose

Post-methods	Lignocellulose	Experimental conditions	H_2 yield (mmol $g_{biomass}^{-1}$)	Ref.
Fermentation	Cassava residues (treated)	Dark fermentation; *Clostridium lentocellum* strain Cel10; 72 h, 37 °C	4.08 mmol $g_{biomass}^{-1}$	[91]
	Corn stover (treated)	Dark fermentation; *Clostridium butyricum*; 20 h; 37 °C	1.2 mmol $g_{biomass}^{-1}$	[92]
	Corn stalk (untreated)	*Thermoanaerobacterium thermosaccharolyticum*; 72 h; 55 °C	6.38 mmol $g_{biomass}^{-1}$	[93]
	Rice straw (treated)	*Enterobacter aerogenes*; 48 h; 37 °C	4.9 mmol $g_{biomass}^{-1}$	[92, 94]
	Sorghum stalk (treated)	*Bacillus subtilis* AuChE413; 24 h; 37 °C	1.8 mmol $g_{biomass}^{-1}$	[92, 95]
Corn stalk (treated)	Photo-fermentation; *Rhodobacter sphaeroides* HY01; 6000 lx	339.5 mL $g_{biomass}^{-1}$	[96]	
Microbial electrolysis	Glucose Galactose Mannose	• Single chamber microbial electrolysis cells: the anodes (2 cm × 1 cm, FuelCells, TX, USA), the cathodes (2 cm × 1 cm, FuelCells, TX, USA) contained 0.5 mg·cm^{-2} Pt catalyst; applied voltage of 0.7 V • Carbohydrate: 3.3 mmol L^{-1}; • The medium solution: 100 mmol L^{-1} ionic strength, consisted of: NH_4Cl (0.31 g L^{-1}), $NaH_2PO_4{\cdot}H_2O$ (5.84 g L^{-1}), $Na_2HPO_4{\cdot}7H_2O$ (15.47 g L^{-1}), KCl (0.13 g L^{-1}), a mineral solution (12.5 mL) and a vitamin solution (12.5 mL).	0.03 m^3 day^{-1} m^{-3} 0.07 m^3 day^{-1} m^{-3} 0.05 m^3 day^{-1} m^{-3}	[97]
	Xylose Arabinose	• Single chamber microbial electrolysis cells: The anodes (2 cm × 1 cm, FuelCells, TX, USA), the cathodes (2 cm × 1 cm, FuelCells, TX, USA) contained 0.5 mg cm^{-2} Pt catalyst; applied voltage of 0.7 V • Carbohydrate: 4 mmol L^{-1}; • The medium solution: 100 mmol L^{-1} ionic strength, consisted of: NH_4Cl (0.31 g L^{-1}), $NaH_2PO_4{\cdot}H_2O$ (5.84 g L^{-1}), $Na_2HPO_4{\cdot}7H_2O$ (15.47 g L^{-1}), KCl (0.13 g L^{-1}), a mineral solution (12.5 mL) and a vitamin solution (12.5 mL).	0.02 m^3 day^{-1} m^{-3} 0.01 m^3 day^{-1} m^{-3}	
Photocatalytic reforming (photo-reforming)	Grass	Pretreatment of grass: washing at 55 °C with H_2O and then with methanol, and drying overnight at 120 °C. Reaction conditions: 0.36 g of washed and dried grass per 200 ml H_2O, 150 mg 0.2% Pt/TiO_2, temperature = 60 °C; 180 min	1.78 ml g_{grass}^{-1}	[25]
	Wooden Branch	• Catalyst: CdS/CdOx QDs • Wooden Branch: 50 mg ml^{-1} • Additive: $Co(BF4)_2$ • Media: KOH (10 M) • Light: AM 1.5G, 100 mW cm^{-2}	5.31 mmol g_{cat}^{-1} h^{-1}; 0.49 mmol $g_{biomass}^{-1}$	[98]
	Sawdust	• Catalyst: CdS/CdOx QDs • Sawdust: 50 mg ml^{-1} • Additive: $Co(BF4)_2$ • Media: KOH (10 M) • Light: AM 1.5G, 100 mW cm^{-2}	0.75 mmol g_{cat}^{-1} h^{-1}; 0.07 mmol $g_{biomass}^{-1}$	
	Sawdust	• Catalyst: activated $^{NCN}CN_x$ (5 mg) • Additive: DuBois-type Ni proton reduction catalyst (NiP, 50 nmol) • Media: potassium phosphate (Kpi, 0.1 M, pH 4.5, 3 mL) • Light: AM 1.5G, 100 mW cm^{-2}	202 μmol g_{CNx}^{-1} h^{-1};	[99]
	Rice husk	• Catalyst: 0.5% Pt/TiO_2; 2 g L^{-1} • Pretreatment of rice husk: used as received. • Light: natural solar light, 450 W m^{-2} in the visible range, and 25 W m^{-2} in the UV.	0.095 mmol g_{cat}^{-1} h^{-1}	[100]

Table 6 (continued)

Post-methods	Lignocellulose	Experimental conditions	H_2 yield (mmol $g_{biomass}^{-1}$)	Ref.
	Alfalfa stems	• Catalyst: 0.5% Pt/TiO_2; 2 g L^{-1} • Pretreatment of biomass: air-dried at room temperature, milled and then sieved at 70 mesh (0.2 mm). • Light: UV-A (366 nm, 4 × 15 W)	0.100 mmol g_{cat}^{-1} h^{-1}	
	Fescue grass	• Catalyst: 0.2% Pt/TiO_2; 0.75 g L^{-1} • H_2O, 60 °C • Pretreatment of the grass: washed with water, pure methanol (to extract the chlorophyll) at 55 °C in a sonic bath, dried at 120 °C overnight and ground in a mortar. • Light: 150 W Xe arc lamp	0.061 mmol g_{cat}^{-1} h^{-1}; 0.076 mmol $g_{biomass}^{-1}$	[25]

perspectives for clean biohydrogen fuel production from waste sources in the future. Comparing to the maximum theoretical hydrogen concentration, the results in Table 6 are still low. Therefore, either fermentation, microbial electrolysis, or photocatalytic reforming route, it is a long-term effort to reach theoretical yield in bioconverting glucose and xylose in lignocellulosic hydrolysate into biohydrogen.

4 Conclusions and future perspectives

In conclusion, the biohydrogen has proven to be a perspective energy source for altering exhausting fossil fuel–based hydrogen. Biohydrogen could be produced by varied renewable biomass sources, leading to minimize and eradicate global warming. Hence, there has been significant progress and effort

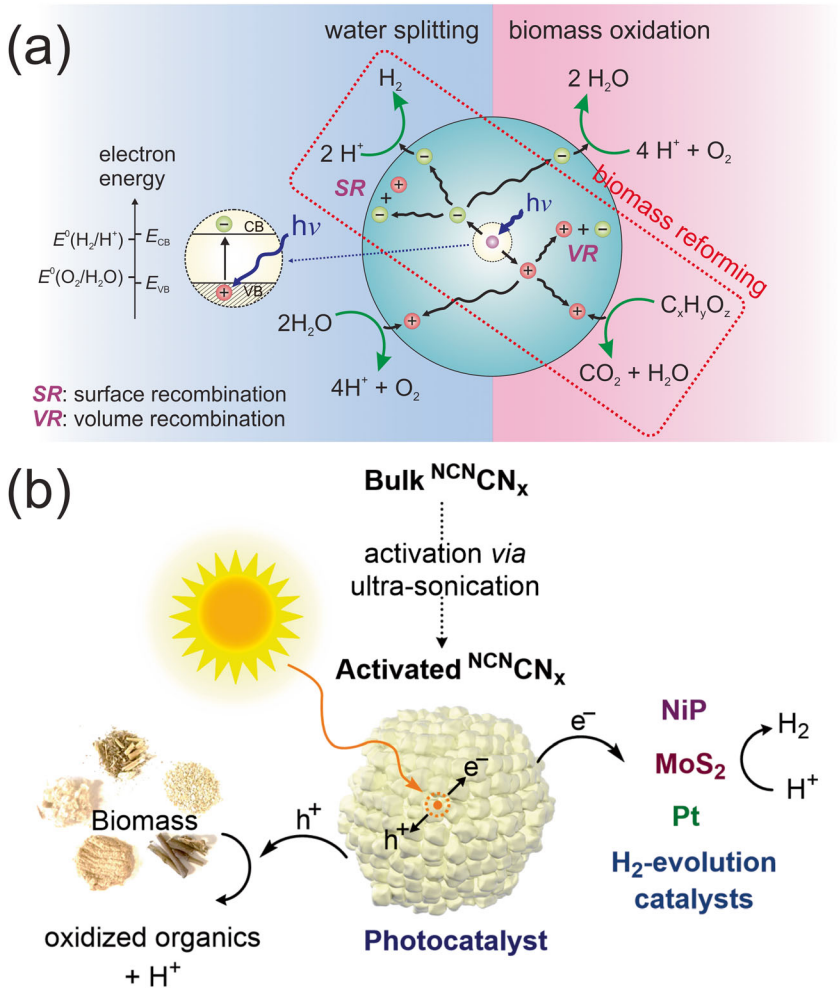

Fig. 6 (a) The scheme of possible reaction pathways by excitation of the photocatalysts with light energy. Reprinted with permission from Huang et al. [105]; license no.: 4922140173731. (b) The possible H_2 generation mechanism via the photo-reforming of lignocellulose over $^{NCN}CN_x$ and H_2 production photocatalysts. Reprinted with permission from Kasap et al. [99]; copyright (2020) American Chemical Society

to explore biohydrogen production at the international and national levels. Herein, lignocellulose-derived monosugars, which are abundant renewable sources, have been considered as a promising feedstock for the second-generation biohydrogen production. However, to obtain these monosugars, these lignocellulose materials need to be pre-treated through complicated processes. Many pre-treating techniques for lignocellulosic material and their advantages and disadvantages, including pretreatment, hydrolysis, and detoxification methods, to figure out an overview picture of recent material treatment methods for biohydrogen production from lignocellulose, have been successfully reviewed and discussed. Besides, the concept to sustainably generate biohydrogen from lignocellulose represents a significant breakthrough. Notably, the selection of different lignocellulose types and processes, which could significantly affect the outcomes, is also favorably highlighted. So far, microbial fermentation (including photo-fermentation and dark fermentation), microbial electrolysis, and photocatalytic reforming are four of the most sustainable post-treatment routes to convert monosugars (mainly glucose and xylose) in lignocellulosic biomass into biohydrogen.

To understand the suitable biomass lignocellulose, pre-treating biomass techniques, and post-methods, and to optimize the operating parameters are required to enhance the conversion efficiencies, low down the cost. Typically, the research and development of designing reactors, understanding kinetics, and revealing reaction pathways are suggested to promote this concept further. Currently, the research on the sustainable generation of biohydrogen via photocatalytic reforming is still in an early stage. It is expected that innovative photocatalytic materials and photocatalytic reaction conditions would enhance the conversion to biohydrogen. For microbial electrolysis, the most challenges of this process are high cost and maintaining the stability of the electrical potential at both the bioanode and biocathode chambers. Therefore, considerable efforts are still needed and deserved further studies to make this concept highly efficient, ecologically friendly, technologically reliable, and relatively low-cost feasible.

Compliance with ethical standards

Conflict of interests The authors declare that they have no competing interests.

References

1. Chen R, Wang YZ, Liao Q, Zhu X, Xu TF (2013) Hydrolysates of lignocellulosic materials for biohydrogen production. BMB Rep 46:244–251
2. Show K-Y, Yan Y-G, Lee D-J (2019) Biohydrogen production: status and perspectives, biofuels: alternative feedstocks and conversion processes for the production of liquid and gaseous biofuels, pp. 693-713
3. Veeravalli SS, Shanmugam SR, Ray S, Lalman JA, Biswas N (2019) Biohydrogen production from renewable resources, advanced bioprocessing for alternative fuels, biobased chemicals, and bioproducts, pp. 289–312
4. Cormos C-C (2011) Hydrogen production from fossil fuels with carbon capture and storage based on chemical looping systems. Int J Hydrog Energy 36:5960–5971
5. Twigg MV, Dupont V (2014) Hydrogen production from fossil fuel and biomass feedstocks, Advances in Hydrogen Production, Storage and Distribution, pp. 43–84
6. Chandrasekhar K, Lee YJ, Lee DW (2015) Biohydrogen production: strategies to improve process efficiency through microbial routes. Int J Mol Sci 16:8266–8293
7. El-Shafie M, Kambara S, Hayakawa Y (2019) Hydrogen production technologies overview. J Power Energy Eng 07:107–154
8. Kamaraj M, Ramachandran KK, Aravind J (2019) Biohydrogen production from waste materials: benefits and challenges. Int J Environ Sci Technol 17:559–576
9. Yadav M, Paritosh K, Vivekanand V (2019) Lignocellulose to bio-hydrogen: an overview on recent developments. Int J Hydrog Energy 45:18195–18210
10. Argun H, Gokfiliz P, Karapinar I (2017) Biohydrogen production potential of different biomass sources, Biohydrogen Production: Sustainability of Current Technology and Future Perspective, pp. 11–48
11. Nguyen V-C, Ke N-J, Nam LD, Nguyen B-S, Xiao Y-K, Lee Y-L, Teng H (2019) Photocatalytic reforming of sugar and glucose into H2 over functionalized graphene dots. J Mater Chem A 7:8384–8393
12. Sutthipattanasomboon C, Wongthanate J (2017) Enhancement of biohydrogen production from starch processing wastewater and further inside its ecosystem disclosed by 16S rDNA sequencing and FISH. Braz Arch Biol Technol 60:e17160260
13. Boddiger D (2007) Boosting biofuel crops could threaten food security. Lancet 370:923–924
14. Popp J, Lakner Z, Harangi-Rákos M, Fári M (2014) The effect of bioenergy expansion: food, energy, and environment. Renew Sust Energ Rev 32:559–578
15. Go AW, Conag AT, Igdon RMB, Toledo AS, Malila JS (2019) Potentials of agricultural and agro-industrial crop residues for the displacement of fossil fuels: a Philippine context. Energy Strategy Rev 23:100–113
16. Passoth V, Sandgren M (2019) Biofuel production from straw hydrolysates: current achievements and perspectives. Appl Microbiol Biotechnol 103:5105–5116
17. Tripathi N, Hills CD, Singh RS, Atkinson CJ (2019) Biomass waste utilisation in low-carbon products: harnessing a major potential resource. NPJ Clim Atmos Sci 2:35
18. Adessi A, De Philippis R (2012) Hydrogen production: photofermentation, Microbial technologies in advanced biofuels production, pp. 53–75
19. Bundhoo ZMA (2019) Potential of bio-hydrogen production from dark fermentation of crop residues: a review. Int J Hydrog Energy 44:17346–17362
20. Hassan AHS, Mietzel T, Brunstermann R, Schmuck S, Schoth J, Kuppers M, Widmann R (2018) Fermentative hydrogen production from low-value substrates. World J Microbiol Biotechnol 34:176
21. Łukajtis R, Hołowacz I, Kucharska K, Glinka M, Rybarczyk P, Przyjazny A, Kamiński M (2018) Hydrogen production from biomass using dark fermentation. Renew Sust Energ Rev 91:665–694
22. Masset J, Calusinska M, Hamilton C, Hiligsmann S, Joris B, Wilmotte A, Thonart P (2012) Fermentative hydrogen production

from glucose and starch using pure strains and artificial co-cultures ofClostridium spp. Biotechnol Biofuels 5:35
23. Mishra P, Krishnan S, Rana S, Singh L, Sakinah M, Ab Wahid Z (2019) Outlook of fermentative hydrogen production techniques: an overview of dark, photo and integrated dark-photo fermentative approach to biomass. Energy Strategy Rev 24:27–37
24. Reungsang A, Zhong N, Yang Y, Sittijunda S, Xia A, Liao Q (2018) Hydrogen from photo fermentation, Bioreactors for Microbial Biomass and Energy Conversion, pp. 221–317
25. Caravaca A, Jones W, Hardacre C, Bowker M (2016) H2 production by the photocatalytic reforming of cellulose and raw biomass using Ni, Pd, Pt and Au on titania. Proc Math Phys Eng Sci 472: 20160054
26. Christoforidis KC, Fornasiero P (2017) Photocatalytic hydrogen production: a rift into the future energy supply. ChemCatChem 9: 1523–1544
27. Da Vià L, Recchi C, Gonzalez-Yañez EO, Davies TE, Lopez-Sanchez JA (2017) Visible light selective photocatalytic conversion of glucose by TiO2. Appl Catal B 202:281–288
28. Imizcoz M, Puga AV (2019) Assessment of Photocatalytic hydrogen production from biomass or wastewaters depending on the metal co-catalyst and its deposition method on TiO2, catalysts, 9
29. Kennedy J, Bahruji H, Bowker M, Davies PR, Bouleghlimat E, Issarapanacheewin S (2018) Hydrogen generation by photocatalytic reforming of potential biofuels: polyols, cyclic alcohols, and saccharides. J Photochem Photobiol A 356:451–456
30. Singh A, Sevda S, Abu Reesh I, Vanbroekhoven K, Rathore D, Pant D (2015) Biohydrogen production from lignocellulosic biomass: technology and sustainability. Energies 8:13062–13080
31. Kucharska K, Rybarczyk P, Holowacz I, Lukajtis R, Glinka M, Kaminski M (2018) Pretreatment of Lignocellulosic materials as substrates for fermentation processes. Molecules 23:2937
32. Jensen CU, Rodriguez Guerrero JK, Karatzos S, Olofsson G, Iversen SB (2017) Fundamentals of Hydrofaction™: renewable crude oil from woody biomass. Biomass Convers Biorefin 7:495–509
33. Bajpai P (2016) Pretreatment of lignocellulosic biomass, Pretreatment of Lignocellulosic Biomass for Biofuel Production, pp. 17–70
34. Ghaemi F, Abdullah LC, Ariffin H (2019) Lignocellulose Structure and the effect on nanocellulose production, Lignocellulose for Future Bioeconomy, pp. 17–30
35. Zoghlami A, Paes G (2019) Lignocellulosic biomass: understanding recalcitrance and predicting hydrolysis. Front Chem 7:874
36. Shahzadi T, Mehmood S, Irshad M, Anwar Z, Afroz A, Zeeshan N, Rashid U, Sughra K (2014) Advances in lignocellulosic biotechnology: a brief review on lignocellulosic biomass and cellulases. Adv Biosci Biotechnol 05:246–251
37. Tayyab M (2018) Bioethanol production from lignocellulosic biomass by environment-friendly pretreatment methods: a review. Appl Ecol Environ Res 16:225–249
38. Rajendran K, Drielak E, Sudarshan Varma V, Muthusamy S, Kumar G (2017) Updates on the pretreatment of lignocellulosic feedstocks for bioenergy production–a review. Biomass Convers Biorefin 8:471–483
39. Sarkar N, Ghosh SK, Bannerjee S, Aikat K (2012) Bioethanol production from agricultural wastes: an overview. Renew Energy 37:19–27
40. Daud Z, Mohd Hatta MZ, Abdul Latiff AA, Awang H (2016) Corn stalk fiber material by chemical pulping process for pulp and paper industry. Adv Mater Res 1133:608–611
41. Flandez J, González I, Resplandis JB, Mansouri N-EE, Vilaseca F, Mutjé P (2012) Management of corn stalk waste as reinforcement for polypropylene injection moulded composites. Bioresources 7: 1836–1849
42. Templeton DW, Sluiter AD, Hayward TK, Hames BR, Thomas SR (2009) Assessing corn stover composition and sources of variability via NIRS. Cellulose 16:621–639
43. Pordesimo LO, Hames BR, Sokhansanj S, Edens WC (2005) Variation in corn stover composition and energy content with crop maturity. Biomass Bioenergy 28:366–374
44. Kosinkova J, Ramirez JA, Ristovski ZD, Brown R, Rainey TJ (2016) Physical and chemical stability of bagasse biocrude from liquefaction stored in real conditions. Energy Fuel 30:10499–10504
45. Guerra A, Filpponen I, Lucia LA, Argyropoulos DS (2006) Comparative evaluation of three lignin isolation protocols for various wood species. J Agric Food Chem 54:9696–9705
46. Pham P, Tuyet-Le D, ThuHuong L, Trong-Anh N (2019) Recycling cassava stem to bioethanol by inoculating a novel xylose–glucose fermenting yeast at high initial concentration. Environ Prog Sustain Energy 39:e13286
47. Sivamani S, Baskar R (2018) Bioconversion of cassava stem to ethanol: oxalic acid pretreatment and co-culture fermentation. Biofuels 9:559–566
48. Held MA, Jiang N, Basu D, Showalter AM, Faik A (2015) Plant cell wall polysaccharides: structure and biosynthesis, Polysaccharides, pp. 3–54
49. Kong-Win Chang J, Duret X, Berberi V, Zahedi-Niaki H, Lavoie JM (2018) Two-step thermochemical cellulose hydrolysis with partial neutralization for glucose production. Front Chem 6:117
50. Tanjore D, Richard TL (2015) A systems view of lignocellulose hydrolysis. In: Ravindra P. (eds) Advances in Bioprocess Technology. Springer, Cham, pp 387–419
51. Li L, Rowbotham JS, Christopher Greenwell H, Dyer PW (2013) Chapter 8 - an introduction to pyrolysis and catalytic pyrolysis: versatile techniques for biomass conversion. In: Suib SL (ed) New and future developments in catalysis. Elsevier, Amsterdam, pp 173–208
52. Kumar AK, Sharma S (2017) Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour Bioprocess 4:7
53. Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2009) Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind Eng Chem Res 48:3713–3729
54. Cunha-Pereira Fd, Hickert LR, Rech R, Dillon AP, Ayub MAZ (2017) Fermentation of hexoses and pentoses from hydrolyzed soybean hull into ethanol and xylitol by *Candida guilliermondii* BL 13. Braz J Chem Eng 34:927–936
55. Kim JH, Block DE, Mills DA (2010) Simultaneous consumption of pentose and hexose sugars: an optimal microbial phenotype for efficient fermentation of lignocellulosic biomass. Appl Microbiol Biotechnol 88:1077–1085
56. Cavka A, Jonsson LJ (2013) Detoxification of lignocellulosic hydrolysates using sodium borohydride. Bioresour Technol 136: 368–376
57. Chen J, Zhang Y, Wang Y, Ji X, Zhang L, Mi X, Huang H (2013) Removal of inhibitors from lignocellulosic hydrolyzates by vacuum membrane distillation. Bioresour Technol 144:680–683
58. Kim D (2018) Physico-chemical conversion of lignocellulose: inhibitor effects and detoxification strategies: a mini review. Molecules 23:309
59. Tanaka K, Koyama M, Pham PT, Rollon AP, Habaki H, Egashira R, Nakasaki K (2019) Production of high-concentration bioethanol from cassava stem by repeated hydrolysis and intermittent yeast inoculation. Int Biodeterior Biodegradation 138:1–7
60. Haldar D, Sen D, Gayen K (2016) A review on the production of fermentable sugars from lignocellulosic biomass through conventional and enzymatic route—a comparison. Int J Green Energy 13: 1232–1253

61. Haldar D, Purkait MK (2020) Lignocellulosic conversion into value-added products: a review. Process Biochem 89:110–133
62. Haldar D, Purkait MK (2020) Thermochemical pretreatment enhanced bioconversion of elephant grass (*Pennisetum purpureum*): insight on the production of sugars and lignin. Biomass Convers Biorefin. https://doi.org/10.1007/s13399-020-00689-y
63. Baruah J, Nath BK, Sharma R, Kumar S, Deka RC, Baruah DC, Kalita E (2018) Recent trends in the pretreatment of lignocellulosic biomass for value-added products. Front Energy Res 6:141
64. Bhatt SM, Shilpa (2015) Lignocellulosic feedstock conversion, inhibitor detoxification and cellulosic hydrolysis – a review. Biofuels 5:633–649
65. Sasmal S, Mohanty K (2018) Pretreatment of lignocellulosic biomass toward biofuel production. In: Kumar S., Sani R. (eds) Biorefining of Biomass to Biofuels. Biofuel and Biorefinery Technologies, vol 4. Springer, Cham, pp. 203–221
66. Achinas S, Achinas V, Euverink GJW (2017) A technological overview of biogas production from biowaste. Engineering 3: 299–307
67. Rezania S, Din MFM, Mohamad SE, Sohaili J, Tai SM, Yusof MBM, Kamy H, Darajeh N, Ahsan A (2017) Review on pretreatment methods and ethanol production from cellulosic water hyacinth. Bioresources 12:2108–2124
68. Tsegaye B, Balomajumder C, Roy P (2019) Microbial delignification and hydrolysis of lignocellulosic biomass to enhance biofuel production: an overview and future prospect. Bull Natl Res Cent 43:51
69. Andlar M, Rezić T, Marđetko N, Kracher D, Ludwig R, Šantek B (2018) Lignocellulose degradation: an overview of fungi and fungal enzymes involved in lignocellulose degradation. Eng Life Sci 18:768–778
70. Su Y, Yu X, Sun Y, Wang G, Chen H, Chen G (2018) Evaluation of screened lignin-degrading fungi for the biological pretreatment of corn Stover. Sci Rep 8:5385
71. Cheah WY, Sankaran R, Show PL, Tg TNB, Ibrahim KW, Chew AC, Chang J-S (2020) Pretreatment methods for lignocellulosic biofuels production: current advances, challenges and future prospects. Biofuel Res J 7:1115–1127
72. Conde-Mejía C, Jiménez-Gutiérrez A, El-Halwagi M (2012) A comparison of pretreatment methods for bioethanol production from lignocellulosic materials. Process Saf Environ Prot 90:189–202
73. Kim TH, Lee YY (2007) Pretreatment of corn stover by soaking in aqueous ammonia at moderate temperatures. Appl Biochem Biotechnol 137–140:81–92
74. Yadav KS, Naseeruddin S, Prashanthi GS, Sateesh L, Rao LV (2011) Bioethanol fermentation of concentrated rice straw hydrolysate using co-culture of Saccharomyces cerevisiae and Pichia stipitis. Bioresour Technol 102:6473–6478
75. Shirkavand E, Baroutian S, Gapes DJ, Young BR (2017) Pretreatment of radiata pine using two white rot fungal strains Stereum hirsutum and Trametes versicolor. Energy Convers Manag 142:13–19
76. Suhara H, Kodama S, Kamei I, Maekawa N, Meguro S (2012) Screening of selective lignin-degrading basidiomycetes and biological pretreatment for enzymatic hydrolysis of bamboo culms. Int Biodeterior Biodegradation 75:176–180
77. Sun YG, Ma YL, Wang LQ, Wang FZ, Wu QQ, Pan GY (2015) Physicochemical properties of corn stalk after treatment using steam explosion coupled with acid or alkali. Carbohydr Polym 117:486–493
78. Ascencio JJ, Chandel AK, Philippini RR, da Silva SS (2019) Comparative study of cellulosic sugars production from sugarcane bagasse after dilute nitric acid, dilute sodium hydroxide and sequential nitric acid-sodium hydroxide pretreatment. Biomass Convers Biorefin. https://doi.org/10.1007/s13399-019-00547-6
79. Kucharska K, Lukajtis R, Slupek E, Cieslinski H, Rybarczyk P, Kaminski M (2018) Hydrogen production from energy poplar preceded by MEA pre-treatment and enzymatic hydrolysis. Molecules 23:3029
80. Haldar D, Gayen K, Sen D (2018) Enumeration of monosugars' inhibition characteristics on the kinetics of enzymatic hydrolysis of cellulose. Process Biochem 72:130–136
81. Haldar D, Sen D, Gayen K (2018) Enzymatic hydrolysis of banana stems (Musa acuminata): optimization of process parameters and inhibition characterization. Int J Green Energy 15:406–413
82. Castaño HP, Reales A JG, Montoya JZ (2015) Enzymatic hydrolysis of cassava stalks pretreated with the alkaline method. Agron Colomb 33:238–243
83. Nuwamanya E, Chiwona-Karltun L, Kawuki RS, Baguma Y (2012) Bio-ethanol production from non-food parts of cassava (Manihot esculenta Crantz). Ambio 41:262–270
84. Sun ZY, Tang YQ, Iwanaga T, Sho T, Kida K (2011) Production of fuel ethanol from bamboo by concentrated sulfuric acid hydrolysis followed by continuous ethanol fermentation. Bioresour Technol 102:10929–10935
85. Dziekońska-Kubczak U, Berłowska J, Dziugan P, Patelski P, Balcerek M, Pielech-Przybylska K, Robak K (2019) Two-stage pretreatment to improve saccharification of oat straw and Jerusalem artichoke biomass. Energies 12:1715
86. Heer D, Sauer U (2008) Identification of furfural as a key toxin in lignocellulosic hydrolysates and evolution of a tolerant yeast strain. Microb Biotechnol 1:497–506
87. Almeida JR, Bertilsson M, Gorwa-Grauslund MF, Gorsich S, Liden G (2009) Metabolic effects of furaldehydes and impacts on biotechnological processes. Appl Microbiol Biotechnol 82: 625–638
88. Jönsson JL, Alriksson B, Nilvebrant N (2013) Bioconversion of lignocellulose: inhibitors and detoxification. Biotechnol Biofuels 6:16
89. Schirmer-Michel AC, Flores SH, Hertz PF, Matos GS, Ayub MA (2008) Production of ethanol from soybean hull hydrolysate by osmotolerant Candida guilliermondii NRRL Y-2075. Bioresour Technol 99:2898–2904
90. Reginatto V, Antonio RV (2015) Fermentative hydrogen production from agroindustrial lignocellulosic substrates. Braz J Microbiol 46:323–335
91. Zhang L, Li Y, Liu X, Ren N, Ding J (2019) Lignocellulosic hydrogen production using dark fermentation by Clostridium lentocellum strain Cel10 newly isolated from Ailuropoda melanoleuca excrement. RSC Adv 9:11179–11185
92. Sun Y, Wang Y, Yang G, Sun Z (2019) Optimization of biohydrogen production using acid pretreated corn stover hydrolysate followed by nickel nanoparticle addition. Int J Energy Res 44:1843–1857
93. Sheng T, Gao L, Zhao L, Liu W, Wang A (2015) Direct hydrogen production from lignocellulose by the newly isolated Thermoanaerobacterium thermosaccharolyticum strain DD32. RSC Adv 5:99781–99788
94. Asadi N, Karimi Alavijeh M, Zilouei H (2018) Biological hydrogen production by Enterobacter aerogenes: structural analysis of treated rice straw and effect of substrate concentration. Int J Hydrog Energy 43:8718–8728
95. Dhanasekar R, Jonesh S (2018) Identification of a novel hydrogen producing bacteria from sugarcane bagasse waste. Biocatal Agric Biotechnol 15:277–282
96. Yang H, Shi B, Ma H, Guo L (2015) Enhanced hydrogen production from cornstalk by dark- and photo-fermentation with diluted alkali-cellulase two-step hydrolysis. Int J Hydrog Energy 40: 12193–12200

97. Catal T (2016) Comparison of various carbohydrates for hydrogen production in microbial electrolysis cells. Biotechnol Biotechnol Equip 30:75–80
98. Wakerley DW, Kuehnel MF, Orchard KL, Ly KH, Rosser TE, Reisner E (2017) Solar-driven reforming of lignocellulose to H2 with a CdS/CdOx photocatalyst. Nat Energy 2:17021
99. Kasap H, Achilleos DS, Huang A, Reisner E (2018) Photoreforming of lignocellulose into H2 using nanoengineered carbon nitride under benign conditions. J Am Chem Soc 140: 11604–11607
100. Speltini A, Sturini M, Dondi D, Annovazzi E, Maraschi F, Caratto V, Profumo A, Buttafava A (2014) Sunlight-promoted photocatalytic hydrogen gas evolution from water-suspended cellulose: a systematic study. Photochem Photobiol Sci 13:1410–1419
101. Miller A, Singh L, Wang L, Liu H (2019) Linking internal resistance with design and operation decisions in microbial electrolysis cells. Environ Int 126:611–618
102. Hamelers HVM, Ter Heijne A, Sleutels THJA, Jeremiasse AW, Strik DPBTB, Buisman CJN (2010) New applications and performance of bioelectrochemical systems. Appl Microbiol Biotechnol 85:1673–1685
103. Liu H, Grot S, Logan BE (2005) Electrochemically assisted microbial production of hydrogen from acetate. Environ Sci Technol 39:4317–4320
104. Miandad R, Rehan M, Ouda OKM, Khan MZ, Shahzad K, Ismail IMI, Nizami AS (2017) Waste-to-hydrogen energy in Saudi Arabia: challenges and perspectives. In: Singh A, Rathore D (eds) Biohydrogen production: sustainability of current technology and future perspective. Springer India, New Delhi, pp 237–252
105. Huang C-W, Nguyen B-S, Wu JCS, Nguyen V-H (2020) A current perspective for photocatalysis towards the hydrogen production from biomass-derived organic substances and water. Int J Hydrog Energy 45:18144–18159