Bioconversion of Hemicelluloses into Hydrogen

Janak Raj Khatiwada, Sarita Shrestha, Hem Kanta Sharma, and Wensheng Qin

Abstract

Hydrogen is a promising alternative to fossil fuels because of its environment-friendly characteristics. It has been used widely in varied sectors such as chemical production, electronic devices, food industries, desulfurization of crude oil, and steel industries. Due to its increasing use and demand, it is essential to develop a cheaper and energy-efficient source of hydrogen production. This review synthesizes and discusses various aspects of hydrogen production methods and processes, the challenges, and economic perspective for sustainable production of biohydrogen. Compared to electrolysis, thermochemical and electrochemical processes, the biohydrogen production is environment friendly and energy efficient. Various factors such as feedstock, pH, temperature, partial pressure of hydrogen, and hydraulic retention time are responsible for the biological process and yield of biological hydrogen production. This review suggests that lignocellulosic biomass is commonly available, cheaper and eco-friendly source of hydrogen production.

Keywords

Hydrogen • Biomass • Pretreatments • Biohydrogen production • Limiting factors

1 Global Energy Demand

The global energy demand increased by 2.9% in 2018 and the annual global energy consumption was estimated at 13,864 million tons of oil equivalent (in 2018). Fossil fuels are regarded as the major drivers of the industrial revolution leading to economic and technological changes in the recent years. In the total energy consumption, fossil fuel alone accounted 85% including oil (34%), natural gas (24%), and coal (27%). Remaining 15% are used from other forms of energy such as nuclear energy (4%), hydroelectricity (7%), and renewable resources (4%) (BP 2019). The high consumption of fossil fuel in recent decades is considered as a major factor for global warming. Also, the recent consumption trend indicates further growth in the increment of greenhouse gas emissions in future. In this context, overcoming the recent energy demand by lowering the emission of greenhouse gas has become a great challenge.

Several researches are ongoing worldwide to discover cheaper, eco-friendly, and alternative renewable energy sources which can minimize the world's carbon footprint. Recent studies revealed that alternative and renewable energy resources could be a better solution for sustainable energy production and energy security in the future because they mitigate greenhouse gas emission (Sharif et al. 2019). Renewable and alternative energy resources are easily available as compared to other energy sources and are derived from solar, hydropower, geothermal, wind, ocean resources, and solid biomass, and others (Ellabban et al. 2014). Compared to other sources of renewable energies, the conversion of biomass for energy production is one of the cheapest and promising alternatives. Moreover, the biomass is readily and widely available and is cheap in terms of investment costs and feasible technology (Macqueen and Korhaliller 2011).

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Large quantity of bio-wastes is produced from different sources including forestry, agriculture, industries, and household solid waste in the world. These biomasses are considered as waste materials particularly in the developing countries and creating several environmental issues (Chen et al. 2017; Worden et al. 2017). However, recent researches have indicated that they can be used as the energy sources to contribute in the global energy production such as bioethanol, biohydrogen, methane, and other value-added products (Limayem and Ricke 2012; Xu et al. 2019; Keskin et al. 2019). Therefore, this review provides recent progress and findings on biohydrogen production from lignocellulosic biomass with a special focus on hemicellulose and discusses the techno-economic bottleneck involved in hydrogen production from plant biomass.

1.1 Classification of Energy Sources

1.1.1 Biomass and Biofuels

Biomass originates from biological materials (plants or animals) that can be used in energy production. Lignocellulosic biomass is a reliable source of energy since the early age of human civilization. Fire is the major energy source from biomass and provides thermal energy to keep warm and be used for cooking food. There are several ways to produce energy from biomass, for example, burning biomass to produce heat in thermal plants (to run the steam engine and generate electricity), and turning feedstocks into liquid biofuels (ethanol) or biogas (hydrogen, oxygen, or methane) (Giampietro et al. 1997). Biofuels are fuel(s) either solid, liquid, or gaseous produced directly or indirectly from biomass (FAO 2004; Lee and Lavoie 2013). Biofuels are grouped as first, second, and third-generation biofuels based on the feedstock used and their technological innovation (Lee and Lavoie 2013).

1.1.2 First-Generation Biofuels

First-generation biofuels are derived from edible food like corn, sugar, and vegetable oil (Aro 2016). Bioethanol is a major by-product produced from the fermentation of edible crops like corn and sugars. Other feedstocks are widely used to produce first-generation bioethanol including barley, potato, sugar-beets, and sugarcane. The first-generation biofuels can blend with petroleum-based fuels and potential improvement on exhaust emissions (Mancaruso et al. 2011). Though the first-generation biofuels have significant positive impacts on environmental pollution and carbon emission, it is not a sustainable energy production because food security versus fuels is its major challenge. Still, it is claimed that biodiesel is not a cost-efficient emission reduction technology. Therefore, more cost-efficient alternative technologies are recommended.

1.1.3 Second-Generation Biofuels

Second-generation biofuels are derived from lignocellulosic biomass such as crop and forest residues, and municipal solid wastes (Begum and Dahman 2015). These biofuels are more sustainable because they are cheap and produced from abundant non-food plant materials. However, their production methods are still quite expensive and have several technical barriers during the bioconversion processes (Mancaruso et al. 2011).

1.1.4 Third-Generation Biofuels

Third-generation biofuels are produced by using algal biomass to manufacture diesel and gasoline (Neto et al. 2019). The microalgae (examples: *Nannochloropsis granulate*, *Spirulina maxima*) can provide different types of renewable biofuel like methane, biodiesel, gasoline, biohydrogen, and jet fuel. Thus, algae can provide a promising source of future fuel and other valuable products (Chowdhury et al. 2019).

2 Lignocellulosic Biomass

Lignocellulosic biomass is the most abundant plant material and is inexpensive, eco-friendly, and abundant renewable resource. It can be used in biofuels, chemicals, and polymer production (Li et al. 2007). There are three major components of lignocellulosic biomass: cellulose (40–60%), hemicellulose (20–40%), and lignin (10–24%) (Sharma et al. 2019). However, the composition of these three primary components varies based on plant type, age, cultivation, and climate conditions.

2.1 Cellulose

Cellulose is the most abundant and major structural component of the plant cell wall (Fig. 1). It is an organized fibrous structure consisting of D-glucose subunits connected by β-1,4 glycosidic bonds (Fengel and Wegener 1989; Pérez et al. 2002). This linkage in carbohydrate or polysaccharide makes cellulose as a straight chain polymer (also called as cellulose microfibrils) (Pérez et al. 2002). The microfibril structure of cellulose is composed of alternating crystalline and amorphous regions (Fengel and Wegener 1989; Nanda et al. 2014). The amorphous form of cellulose is susceptible to enzymatic decomposition (Kumar et al. 2009).

2.2 Hemicellulose

It is the second most abundant polysaccharide found in plant biomass (Fig. 1). Hemicellulose is composed of short lateral

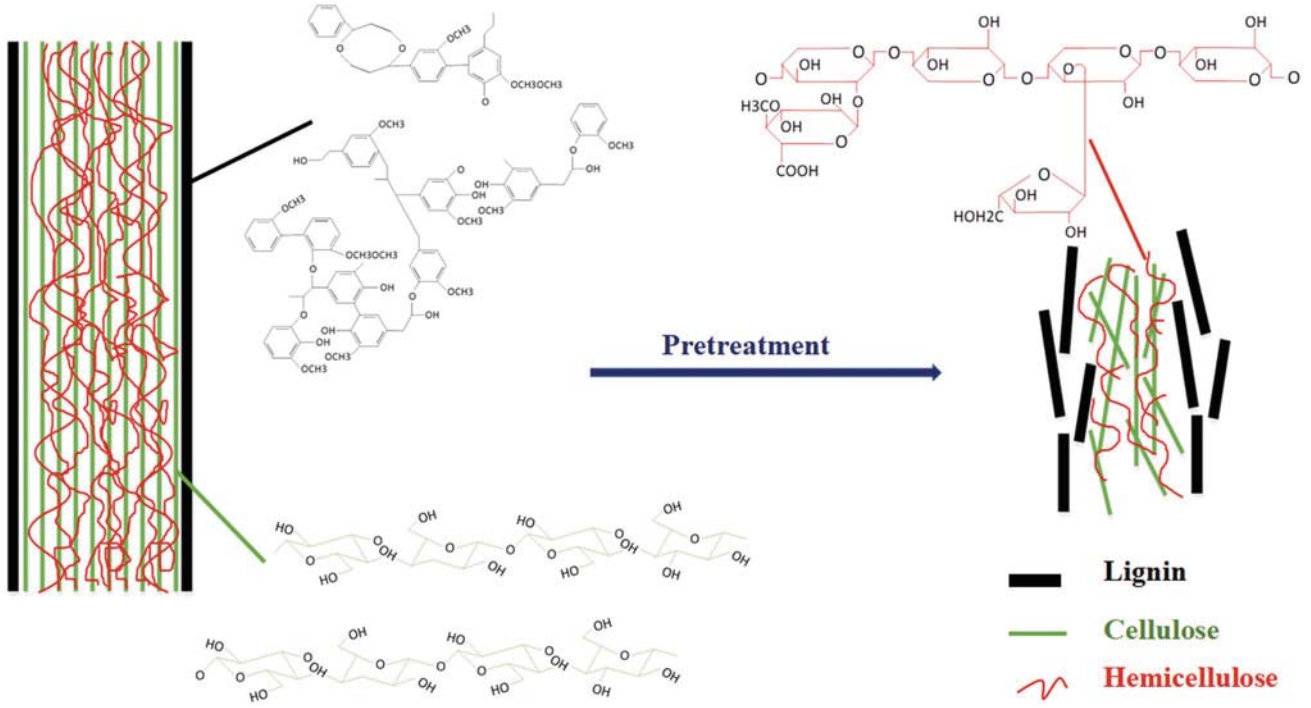

Fig. 1 Diagrammatic representation of the lignocellulosic biomass and the role of pretreatment in the bioconversion

chains of different hexose and pentose sugars (such as xylose, mannose, galactose, rhamnose, and arabinose) and uronic acids (Lin et al. 2015). Glucuronoxylan and glucomannan are the principal components of hardwood and softwood hemicellulose, respectively (Pérez et al. 2002).

2.3 Lignin

Lignin is a complex, branched phenolic polymer containing three phenylpropanolic monomers linked by carbon-carbon and aryl-ether bonds (Lu et al. 2017; Upton and Kasko 2016). Lignin accounts for 30% of total organic carbon found on Earth (Upton and Kasko 2016). It is an aromatic natural polymer found in all terrestrial and some of the aquatic plants (Guragain et al. 2015). It acts as a potentially renewable resource for energy and aromatic chemical production. The lignin provides structural support, impermeability, transport water and nutrients, and protection against chemical and pathogen attack (Polo et al. 2020; Bonawitz and Chapple 2010).

3 Bioconversion of Lignocellulosic Biomass

Each year several tons of lignocellulosic wastes are produced from different sources including forestry and agricultural biomass, paper and food industries, and municipal solid waste (Limayem and Ricke 2012; Dashtban et al. 2009). Even today, these biomasses are considered as waste materials in developing countries which are creating several environmental issues (Chen et al. 2017; Worden et al. 2017). However, recent data suggested that lignocellulosic biomasses can be successfully converted into biofuels (Putro et al. 2016). The global bioethanol production has dramatically increased since 2000 and reached up to 72.06 Billion Gallons per year in 2017 (EIA 2020) (Fig. 2). More than 84% of the global ethanol fuel production (22.86 out of 27.06 Billions of

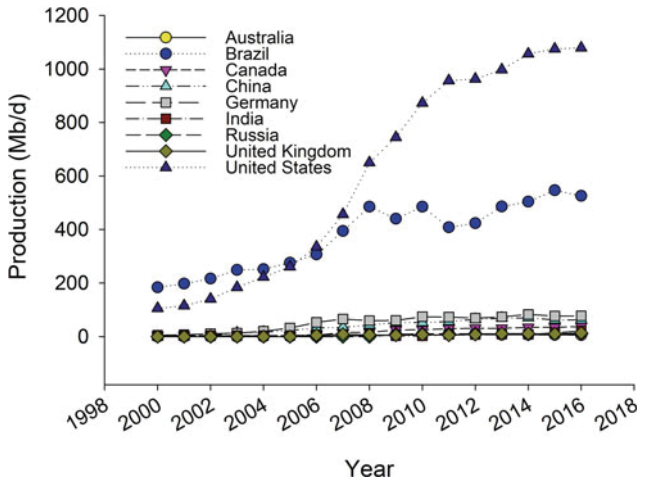

Fig. 2 Biofuel production by countries from 2000 to 2017 (*Data source* EIA (2020))

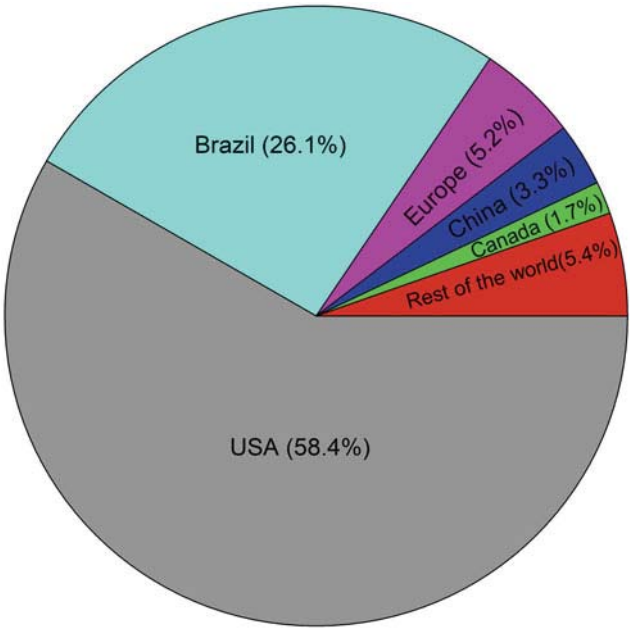

Fig. 3 Biofuel production by countries in the year 2017 (*Data source* EIA (2020))

Gallons) was concentrated in two countries, USA (15.8) and Brazil (7.06) in 2017 (EIA 2020) (Fig. 3).

4 Pretreatment

The lignocellulosic biomass has a property to resist against chemicals and biological degradation (Polo et al. 2020). The structural complexity of the plant cell wall hinders the pretreatment process (Fig. 1) (Jeoh et al. 2017). Pretreatment of biomass is an essential tool in the bioconversion processes in which the structure of cellulosic biomass is converted to be more accessible for enzymatic and microbial digestion (Galbe and Zacchi 2012; Zheng et al. 2014). In this process, the complex structure of carbohydrate polymers is converted into fermentable sugars. Several studies have been carried out for the enhancement of the digestibility process of lignocellulosic biomass for the efficient conversion of biopolymers to biofuel (ethanol, methane and, hydrogen) and other products (Sharma et al. 2019; Koupaie et al. 2019). The major goal of pretreatment is to disintegrate the lignocellulosic biomass into its three major components; cellulose, hemicellulose, and lignin. Broadly the pretreatment methods can be divided into physical, chemical, physicochemical, and biological methods or their combinations (Table 1) (Xu et al. 2019; Sindhu et al. 2016).

5 Hydrogen as a Promising Source of Energy

Hydrogen is considered as a promising alternative source of energy. It can be generated from natural and bioresources (Jiang et al. 2019). It is a colorless, odorless, tasteless, and highly abundant gas. Hydrogen is a clean and non-toxic renewable energy (Hosseini and Wahid 2016). There has been increasing demand for hydrogen in different sectors, for example, in the production of chemicals, electronic devices, food industries, desulfurization of crude oil in oil refineries, and steel industries (Glenk and Reichelstein 2019; Nicita et al. 2020). It is reported that about 95% of current hydrogen production is based on fossil fuel (IRENA 2018; Thomas et al. 2018). The most common ways of hydrogen production are steam-methane reforming, non-catalytic partial oxidation of fossil fuels, hybrid form, and electrolysis (chlor-alkali) processes (Muradov 2017). However, these methods are highly cost-inefficient, requiring sophisticated technology for storage and distribution. Therefore, researchers are struggling to find the renewable and environmentally friendly sources of hydrogen production. Consequently, they have successfully uncovered the bioconversion process of lignocellulosic biomass (Xu 2007) and solid wastes (Lay et al. 1999) into hydrogen in the recent decades. In the initial stage of the conversion process, plant biomass and organic wastes are converted into methane by the application of chemical reactions and bacteria. Then organic matters are hydrolyzed and fermented into fatty acids, which are then converted into acetate and hydrogen.

Bioconversion of lignocellulosic biomass into hydrogen has several positive impacts in sustainable energy production, global energy use, and maintaining a sustainable environment. Following significant advantages of producing hydrogen as an energy resource can be highlighted:

- Hydrogen is clean and produces water vapor after combustion (Stern 2018).
- The combustion of hydrogen is about 50% more efficient than gasoline (Kim et al. 2018).
- Hydrogen gas has a higher energy yield (122 kJ/g) compared to other hydrocarbon fuels (Kapdan and Kargi 2006).
- Hydrogen battery can be used as future power for automobiles (T-Raissi and Block 2004).
- Hydrogen gas can be easily stored as a metal hydride such as magnesium hydride, sodium aluminum hydride, lithium aluminum hydride, palladium hydride, etc. (Jain 2009).

Table 1 Comparison of pretreatment methods of lignocellulosic biomass

Pretreatment	Functions	References
Physical pretreatment		
Milling	Breaks down the structure of lignocellulosic biomass, size reduction, decrease crystallinity of cellulose	Bai et al. (2018)
Pyrolysis	Decomposition of cellulose into H_2, CO, and other carbon residues at high temperatures (>300 °C)	Al Arni (2018)
Microwave	Breakdown of lignocellulose and increase the enzymatic process	Liu et al. (2018)
Extrusion	Disruptions of lignocellulose in high temperature (>300 °C)	Wahid et al. (2015)
Ultrasonication	Breakdown of the lignin layer and disrupt the amorphous cell	He et al. (2017)
Chemical pretreatment		
Acid	Breakdown lignin and other polymers under high temperature	Lloyd and Wyman (2005)
Alkali	Breakdown lignin and other polymers under high temperature	Sun et al. (2016)
Ionic liquids	Cations and anions help to solubilize the cellulose and lignin	Swatloski et al. (2002)
Organosolv	Separation of cellulose by dissolving most lignin and hemicellulose with or without addition of a catalyst	Yu et al. (2018)
Deep eutectic Solvents	Solubilize polysaccharides, accelerate cellulose extraction, nanofibrillation or nanocrystalization	Zdanowicz et al. (2018)
Physicochemical pretreatments		
Steam explosion	Hemicellulose degradation by the application of heat in the form of pressurized steam	Chen and Liu (2015)
CO_2 explosion	Disruption of hemicellulose and lignin, enhance enzymatic hydrolysis	Morais et al. (2015)
Liquid hot water	Hydrolyzes hemicellulose and breakdown of lignin at high water temperature and pressure	Zhuang et al. (2016)
Biological pretreatments		
Whole cell	Breakdown of lignin	Hammel and Cullen (2008)
Enzymatic pretreatment	Enzymatic degradation of lignin	Zámocký et al. (2014)

5.1 Thermochemical Routes for Hydrogen Production from Biomass

Broadly, there are two ways of hydrogen production from lignocellulosic biomass: they are thermochemical and biochemical methods (Fig. 4). Biochemical methods require starch or sugar enriched feedstock whereas various ranges of lignocellulosic biomass can be utilized in thermochemical methods (Basu 2013). Moreover, thermochemical methods are much energy and cost-efficient and faster compared to biochemical routes. Thermochemical process uses heat from various resources, such as natural gas, coal, or biomass to convert the lignocellulosic biomass into hydrogen. There are three types of thermochemical processes (1) Pyrolysis, (2) Liquefaction, and (3) Gasification. Three methods, feedstock used, condition, product yield, major advantages, and disadvantages are summarized in Table 2.

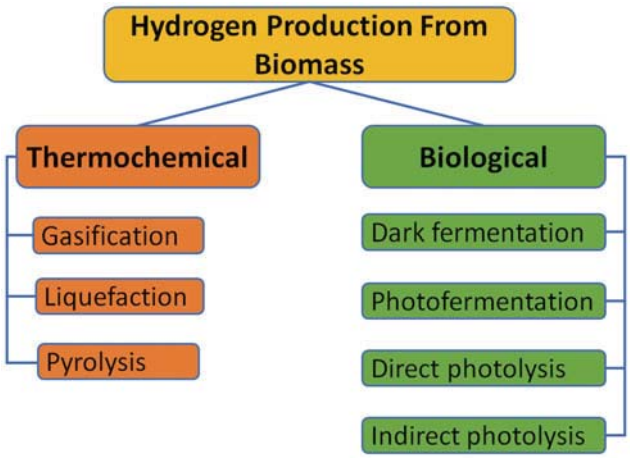

Fig. 4 Methods of hydrogen production from biomass

Table 2 Summary of pretreatments of biomass via pyrolysis and gasification

Method	Feedstock	Process condition	H_2 yield	Major advantages	Major disadvantage	References
Fast pyrolysis	Forest pinewood waste	500–600 °C	117 g per kg of biomass	Simple process	Lower yield of biofuel	Arregi et al. (2016)
Flash pyrolysis	Rice husk and sawdust	800 and 900 °C	0.267 Nm^3/kg	Easy handling process	Less economic	Sun et al. (2010)
Slow pyrolysis	Cellulose fibers and lignin	600 °C	Xylan—0.30%, Cellulose—0.08%, Lignin—0.33% of biomass	Low-value energy product	Not profitable	Giudicianni et al. (2013)
Air gasification	Pine sawdust	870 °C	High temperature favored higher H_2 production	Low-value energy product	Lower yield of hydrogen	Lv et al. (2007)
Air and oxygen/steam gasification	Pine wood blocks	886 °C	30.51% of total gas produced	Higher yield in low energy consumption		Lv et al. (2007)
Supercritical water gasification	Sawdust and municipal solid waste	375 °C and 22 MPa	0.12% of total biomass	Simple process	High processing costs	Castello et al. (2017)

5.1.1 Pyrolysis

Pyrolysis is the conversion of biomass or any carbonaceous feedstocks in anaerobic condition to produce charcoal, bio-oil, and biogas at a pressure of 0.1–0.5 MPa and a temperature of 500–900 °C (Ni et al. 2006; Bičáková and Straka 2012). The major purpose of the pyrolysis is to break down the polymeric molecules into shorter molecular weight compounds. Biomass pyrolysis is categorized into conventional (slow), vacuum, fast, and flash pyrolysis. The major differences between slow and fast pyrolysis are the heating rates (time) and maximum reaction temperatures (Al 2018). The differences in time and temperature significantly affect production of biofuels and other products. Slow pyrolysis produces primarily gas while fast pyrolysis generates biofuel (Brown et al. 2011; Demirbas 2016). Therefore, fast pyrolysis is cost, time, and energy efficient in the conversion of biomass. Pyrolytic decomposition of biomass can be illustrated by the following equation (Eq. 1) (Demirbas 2016):

$$\text{Biomass} + \text{Energy} \rightarrow H_2 + CO + CO_2 + \text{HC gases} + \text{Tar} + \text{Char} \quad (1)$$

i. Fast pyrolysis

The biomass feedstock is heated rapidly in anoxic condition. There are three main products of fast pyrolysis: bio-oil, gas, and char. Tar (47.13%) is the major product of fast pyrolysis followed by char (28.33%), losses (13.21%), and gases (11.33%) respectively at 653 K (Al 2018). The major gases include H_2, CH_4, CO, CO_2, and other depending on the feedstocks used for pyrolysis (Demirbas 2016).

ii. Slow pyrolysis

It is the conventional form of pyrolysis in which the production of charcoal or char is the major by-product. The plant biomass is heated slowly in an anaerobic condition to a relatively low temperature (about 400 °C) over an extended period (Basu 2013). According to Al Arni (2018) char (37.64%) is the major product of slow pyrolysis followed by tar (26.11%), gas (25.10%), and losses (11.15%) at 753 K.

iii. Flash pyrolysis

Flash pyrolysis is also called very fast pyrolysis. In this process biomass is rapidly heated (above 1000 °C/s) in an anoxic condition. The main product of the flash pyrolysis is biofuel (about 70–75% of biomass) with 15–25% of biochar residues (Basu 2013).

5.1.2 Gasification

In comparison to the pyrolysis processes, the gasification process aims to maximize the conversion of a solid biomass into usable gases. The gasification process converts organic biomass into hydrogen and other products without combustion. In this process, biomass is heated at high temperatures (>700 °C) provided with a regulated amount of oxygen and steam. This process produces carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2) (Eq. 2) (Balat and Kırtay 2010). Biomass gasification takes place in a complex chain of chemical reactions. Usually, this process is

completed through the following stages: drying, pyrolysis, char, and tar gasification. Different types of biomass materials such as waste wood, sawdust, and agricultural waste can be used to produce hydrogen via gasification (Basu 2013).

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other} \quad (2)$$

5.1.3 Liquefaction

Liquefaction (hydrothermal liquefaction) is a process of conversion of lignocellulosic biomass into bio-liquid at a temperature of 280–370 °C and pressure of 10–25 MPa in the absence of oxygen (Gollakota et al. 2018). The major goal of this process is to break down the solid biopolymeric structure into liquid components (Elliott et al. 2015). During the conversion process many complex reactions take place and convert biomass into crude oil-like products (Behrendt et al. 2008). There are major two types of process mechanism based on the nature of feedstock namely dry feedstock (lignocellulose biomass) and wet feedstock (algal biomass) (Elliott et al. 2015). Lower hydrogen yield is the major limitation of this method.

5.2 Biological Routes for Hydrogen Production

There has been growing interest in bioconversion of waste products and biomass to produce biofuels and biohydrogen. Biohydrogen production is considered as an eco-friendly and inexhaustible process than electrolysis, thermochemical, and electrochemical processes (Kırtay 2011). In biological processes the feedstocks are catalyzed by microorganisms under atmospheric pressure and at an ambient temperature. Biohydrogen production methods are broadly categorized as light-dependent and light-independent processes (Ding et al. 2016). Light-dependent processes can be further classified into direct biophotolysis, indirect biophotolysis, and photo-fermentation. Light-independent processes are also called dark fermentation (Table 3).

5.2.1 Direct Biophotolysis

Biohydrogen production through biophotolysis is carried out by photosynthetic organisms such as microalgae and cyanobacteria (Eq. 3) (Eroglu and Melis 2011). In this process, autotrophs decompose water into hydrogen and oxygen in the presence of sunlight.

$$2H_2O \ \text{Sun light} \rightarrow 2H_2 + O_2 \quad (3)$$

Table 3 Review of biological hydrogen process and its prospects

Methods	Organisms	H_2 production	Advantages	Disadvantages	References
Direct biophotolysis	Cyanobacteria and algae	1.1 mmol/l-h	•H_2 production from hydrolysis •Lignocellulosic biomass as substrate Easy to operate	•Low H_2 production rate •Extremely light dependent •Low conversion efficiency from light Product contains CO_2 or O_2	Sun et al. (2019), Tamburic et al. (2011)
Indirect biophotolysis	Cyanobacteria	0.0114 kg H_2/kg biomass	•H_2 production from water and sunlight •Lignocellulosic biomass as substrate •Easy to operate	•Low photochemical efficiency •O_2 is inhibitory to nitrogenase	Sveshnikov et al. (1997), Hallenbeck and Benemann (2002)
Photo-fermentation	Photosynthetic bacteria	2.41 mol H_2/mol glucose	•Sunlight as source of energy •Lignocellulosic biomass as substrate	•Highly light dependent •Low H_2 production	Toledo-Alarcón et al. (2018), Ghirardi et al. (2000)
Dark fermentation	Obligate or facultative anaerobic fermentative bacteria	32 mmol/Lglucose	•H_2 can be produced without light •Wide spectrum waste can be used	•Low H_2 yield •Large production of by-product gases	Li and Fang (2007), Ghirardi et al. (2000)

The hydrolysis is carried out into two different photosynthesis stages: photosystem I (PSI) and photosystem II (PSII). In photosystem I (PSI), production of the reductant of CO_2 taken place whereas in photosystem II (PSII) split water into H_2 and O_2 (Bolatkhan et al. 2019). In direct photolysis, various green algae (such as *Chlamydomonas reinhardtii*, *Chlorococcumlittorale*, *Chlorella fusca*, *Platymonassubcordiformis*, *Scenedesmus obliquus*etc.) (Fan et al. 2016; Guan et al. 2004) and cyanobacteria (*Anabaena cylindrical, Oscillatoria brevis*, *Nostocmuscorum,* etc.) are widely used for hydrogen production (Das and Veziroglu 2008; Dutta et al. 2005).

Water is used as the primary feedstock in the direct biophotolysis method which is inexpensive and available everywhere. On the other side, hydrogen production is prohibited by the suppressive effect of oxygen as a by-product of photosynthesis and enzymatic catalysis which is the major drawback of this method (Table 3) (Sun et al. 2019). Moreover, this process yields less hydrogen and cost-inefficient in the industrial-scale production (Sakurai and Masukawa 2007).

5.2.2 Indirect Biophotolysis

Indirect biophotolysis is carried out in two steps: photosynthesis and fermentation. Firstly, the synthesis of carbohydrates takes place under the light (Eq. 4). Secondly, the hydrogen is produced from carbohydrates via anaerobic dark fermentation (Eq. 5) (Hallenbeck and Benemann 2002; Kossalbayev et al. 2020).

$$6H_2O + 6CO_2 \text{ Sun light} \rightarrow C_6H_{12}O_6 + 6O_2 \quad (4)$$

$$C_6H_{12}O_6 + 12H_2O \text{ Sun light} \rightarrow 12H_{12} + 6CO_2 \quad (5)$$

Cyanobacteria play a major role in the production of hydrogen in indirect biophotolysis processes. It possesses major enzymes such as nitrogenase and hydrogenase which helped in metabolic functions for the hydrogen (Hallenbeck and Benemann 2002; Kossalbayev et al. 2020).

5.2.3 Photo-Fermentation

In this process, lignocellulosic feedstocks are decomposed into hydrogen and carbon dioxide by using photosynthetic microorganisms such as *Rhodobacter* sp. in the presence of sunlight and organic acids. Photo-fermentation occurs under oxygen deficient condition with the optimal temperature of 30–35 °C and pH 7.0 (Eq. 6) (Argun and Kargi 2011). In this process wide range of organic wastes such as fruits and vegetable wastes or other lignocellulosic wastes can be used as substrate for the production of biohydrogen (Özgür et al. 2010; Fascetti and Todini 1995).

$$CH_3COOH + 2H_2O \text{ Sun light} \rightarrow 4H_2 + 2CO_2 \quad (6)$$

5.2.4 Dark Fermentation

Dark fermentation is environmentally friendly and widely used method for biohydrogen production from organic feedstocks. This process is undertaken in a dark and anaerobic environment in which anaerobic bacteria convert carbohydrate-rich substrates into hydrogen (Toledo-Alarcón et al. 2018). This process is carried out by different groups of bacteria such as *Enteric* and *Clostridia* sp. (Khanna and Das 2013). In the dark fermentation, the first step is the glycolysis process in which glucose is fermented to pyruvate. Then, under the anaerobic environment, pyruvate is oxidized to acetyl-CoA, CO_2, and H_2 (Li and Fang 2007). Compared to other biological production methods, dark fermentation process is cost-effective, higher hydrogen production rate, and faster conversion efficiencies. This process can utilize a wide range of organic feedstocks including municipal wastes, agriculture, and forest residues (Ghimire et al. 2015).

6 Metabolic Pathway of Hydrogen Production

Hydrogen can be produced via biophotolysis, photo-fermentation, and dark fermentation (Ding et al. 2016). Although biophotolysis by green microalgae and cyanobacteria is a highly desirable process, the photochemical efficiency is low due to oxygen inhibition on hydrogenase (Oh et al. 2013). Microbial fermentation (including dark fermentation and photo-fermentation) could be one of the potential alternatives to produce biohydrogen. However, except for the glucose, lignocellulosic biomass has not been studied extensively for the hydrogen production due to structural complexity of plant biomass. Usually, a pretreatment of lignocellulosic biomass is an essential step before hydrolysis to convert a complex biopolymer into fermentable sugars (glucose and xylose). Hydrolysis of cellulosic biomass is catalyzed by synergistic effect of cellulase-endoglucanase, cellobiohydrolase, and β-glucosidase to form glucose, whereas the hemicellulosic components are catalyzed by hemicellulolytic enzymes such as endo-xylanase, exo-xylanase, and β-xylosidase to form xylose (Sharma et al. 2019). These sugars can be utilized further in hydrogen production. However, the hydrolysis of lignocellulosic biomass often produces some inhibitory compounds such as phenolic and other aromatic compounds, levulinic acid, aliphatic acids, and furan aldehydes, etc. which inhibit the microbial growth and hinder the downstream processing of bioproducts (Jönsson et al. 2013; Jönsson and Martín 2016). Thus, a direct bioconversion (without pretreatment) of cellulosic and hemicellulosic biomass for hydrogen production is gaining popularity due to its environmental and economic benefit. Some thermophilic

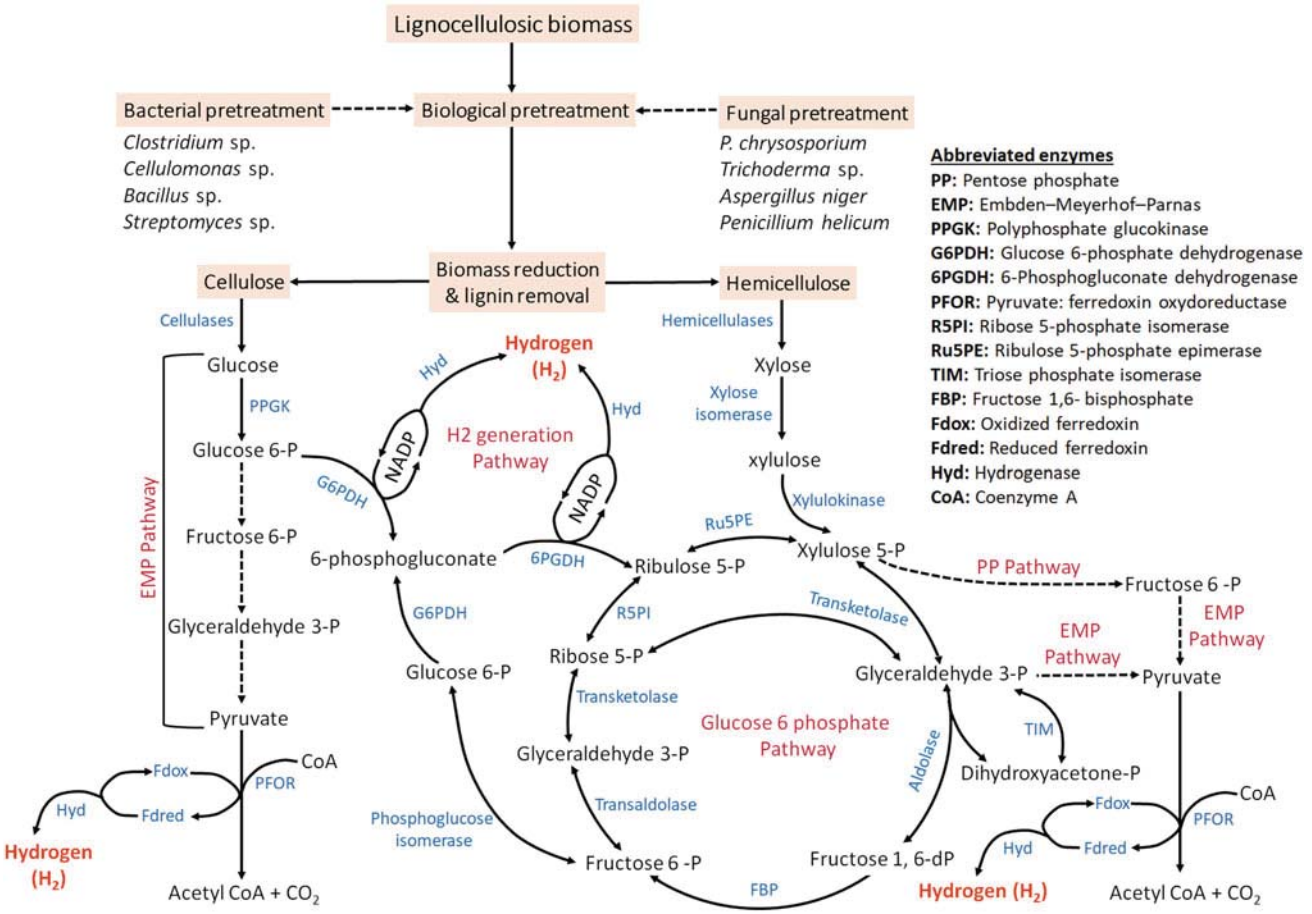

Fig. 5 Major metabolic pathways of hydrogen biosynthesis from lignocellulosic biomass (adopted and modified from Rollin et al. (2015)). The enzymes and pathways are in blue and red-colored text, respectively. The dashed arrows indicate the multi-steps metabolic pathway. Few representative bacteria, fungi, and abbreviated enzymes are included in the figure legend

bacteria including *Clostridium* sp., *Caldicellulosiruptor saccharolyticus, Thermoanaerobacterium* sp., *Thermotoga-maritima* sp. *Pyrococcusfuriosus* sp., etc. can produce hydrogen directly from various plant polymers (Cao et al. 2014; Ren et al. 2008; Willquist et al. 2011; Verhaart et al. 2010). When grown in polymeric biomass, these bacteria utilize various hydrolytic enzymes and hydrogenases for hydrogen production (Oh et al. 2013). Based on the literature reviewed (Rollin et al. 2015; Reginatto and Antônio 2015; Yu and Takahashi 2007), we reconstruct the potential metabolic pathways for hydrogen production (Fig. 5). Reginatto and Antônio (2015) outlined the hydrogen production through fermentation pathways using *Escherichia coli* and *Enterobacteriaceae* and several enzymes via Embden–Meyerhof–Parnas (EMP) pathway to form pyruvate. The pyruvate is further catalyzed by ferredoxin oxydoreductase and converted into acetyl-CoA and then to acetate with the release of hydrogen and carbon dioxide under anaerobic conditions. The enzyme hydrogenase plays a key role at the final stage of hydrogen production. Rollin et al. (2015) proposed another hydrogen generation pathway from lignocellulosic biomass in which bioconversion cellulosic and hemicellulosic biomasses in hydrogen production are resulted in formation of monomeric sugars—glucose and xylose produced after hydrolysis of plant biomass. These sugars are subjected to phosphorylation by the action of polyphosphate. The nicotinamide adenine dinucleotide phosphate (NADPH) is further catalyzed by dehydrogenases and hydrogenase to produced hydrogen. Here the nonoxidative pentose phosphate pathway and partial glycolysis pathways recycle the ribulose, 5-xylulose, and 5-phosphates to glucose 6-phosphates that ultimately used in the production of hydrogen (Rollin et al. 2015).

7 Factors Affecting Hydrogen Production in Dark Fermentation

7.1 Feedstock

Organic feedstocks play a major role in the production of biohydrogen from dark fermentation methods. Glucose and sucrose rich feedstock are model substrates for biohydrogen production (Ghimire et al. 2015). Still, complex substrates such as municipal solid waste, forestry and agricultural biomasses (such as dead wood, corn stalks, wheat straw, and rice straw) and wastages from food processing industries (e.g., cheese whey, oil mills, and animals dungs) have been widely used in dark fermentation process to produce hydrogen (Keskin et al. 2019; Kargi et al. 2012; Mohammadi et al. 2011; Chen et al. 2012).

7.2 pH

pH is a major factor that regulates the enzymatic functions thereby affecting the metabolic pathway of organisms to produce hydrogen (Ghimire et al. 2015). In the dark fermentation process, several facultative organisms have been used to produce hydrogen via glycolysis (Tao et al. 2007). This enzymatic pathway of the hydrogen production is highly sensitive to the pH. Tao et al. (2007) reported that maximum hydrogen yield at medium pH level (pH = 6). Thus, pH level significantly affects the hydrogenase enzyme activity. If the medium concentration becomes acidic, pH level gets reduced which directly shifts enzymatic metabolism towards the conversion of acid into alcohol. At the lower pH level, hydrogen yield decreases sharply due to the production of acidic metabolites such as carboxylic acid, acetic acid, and formic acid. Similarly, Zagrodnik and Laniecki (2015) reported the reduction of the production of H_2 with increasing pH level.

7.3 Temperature

Temperature regulates the bacterial growth, rate of biohydrogen production, and microbial metabolisms in anaerobic fermentation processes. The selection of optimal temperature and organisms used for the fermentation process depends on feedstock types. Due to the complexities of the lignocellulosic biomass, there is considerable variation in operating temperature. Thus, optimal temperature selection is important based on bacteria/organisms used during fermentation. Organisms (anaerobic bacteria) that have been used for dark fermentation are classified into different groups (such as psychrophiles, mesophiles, thermophiles, extreme thermophiles, and hyperthermophiles) based on the optimal temperature in which particular organism perform higher microbial activities and also accelerate the bioconversion rate of feedstocks (Levin et al. 2004; Alvarado-Cuevas et al. 2015; Boileau et al. 2016). Among them, mesophilic condition (temperature range: 25–45 °C, e.g. *Clostridium saccharobutylicum*) is the most favorable temperature range for the fermentative biohydrogen production (Li and Fang 2007). In contrast, thermophilic (45–65 °C) and extreme-thermophilic (65–80 °C) bacteria can perform effectively during fermentation of the diversified feedstock such as buffalo manure, cheese whey, and sludge (Ghimire et al. 2015; Verhaart et al. 2010; Pakarinen et al. 2008). However, biohydrogen production from extreme-thermophilic conditions requires higher energy input (Hallenbeck 2005).

7.4 Hydrogen Partial Pressure (HPP)

HPP is a pressure created by hydrogen gas inside the reactor system (Hawkes et al. 2007). When hydrogen started to accumulate inside the reactor, the partial pressure of hydrogen increases and subsequently decreases the production of hydrogen. Consequently, metabolic pathway of hydrogen production shifts and starts to the accumulated other byproducts such as ethanol, acetone, and lactic acid, (Ghimire et al. 2015; Hawkes et al. 2007). Lee et al. (2012) reported that reduction of the partial pressure during the hydrogen metabolism in dark fermentation increases the production of H_2.

7.5 Hydraulic Retention Time

Hydraulic retention time (or fermentation time or hydraulic loading) is the average number of time (days) that a feedstock remains in a storage unit (digester/bioreactor). Hydraulic retention time is calculated by dividing bioreactor volume (gallons) by the feed volume (gal/day) (Kim et al. 2013). Higher hydrogen production is highly correlated with shorter retention time (Zhang et al. 2013).

8 Conclusion

Lignocellulosic biomass has been extensively used for biohydrogen production. It consists of biopolymer components such as cellulose, hemicellulose, and lignin. Glucose and xylose are the final products after the appropriate pretreatment of hemicellulose or lignocellulosic biomass. Different pretreatment methods, for example, physical, chemical, and

biological have been employed to convert the complex structure of carbohydrate polymers into fermentable sugars. Biological pretreatments of lignocellulosic feedstock are the most desirable methods compared to conventional pretreatment methods which are cost-inefficient and produce undesirable inhibitors. Among the different methods of hydrogen production, the biological route is cheaper and eco-friendly. Biological hydrogen production process is highly affected by several factors such as feedstock, pH, temperature, the partial pressure of hydrogen, and hydraulic retention time. Further improvement in genetic engineering and biotechnologies are needed for more efficient and cost-effective biological pretreatment and low-cost conversion of hemicellulose into hydrogen and other value-added products.

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