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# Bio-hydrogen and Methane Production from Lignocellulosic Materials

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## Abstract

This chapter covers the information on bio-hydrogen and methane production from lignocellulosic materials. Pretreatment methods of lignocellulosic materials and the factors affecting bio-hydrogen production, both dark- and photo-fermentation, and methane production are addressed. Last but not least, the processes for bio-hydrogen and methane production from lignocellulosic materials are discussed.

**Keywords:** anaerobic digestion, pretreatment, biomass, bioconversion, fermentation process, bio-hydrogen, methane

## 1. Introduction

The need for energy has continuously been a major issue in human society. Energy use per capita has been increasing at an average rate of 21.5 kg of oil equivalent annually since the year 2000 (value calculated from [1]). Increase in energy demands leads to the search for alternative sources for energy production. Biomass, as the fourth largest energy source after coal, oil, and natural gas, is a very promising resource for energy production due to its renewability and versatility [2]. Biomass is biologically originated materials or simply any materials that are not fossilized. Supplies of biomass could be from forestry, agriculture, and wastes. They could be used directly to produce energy by burning or could be refined to produce biofuels in the form of solid, liquid, or gas [3].

Lignocellulosic biomass is the biomass with the structure that is composed of lignin, hemicellulose, and cellulose. They can be divided into woody and non-woody biomass. Woody biomass can be further categorized into hardwoods and softwoods, which differ in their reproduction; angiosperm for hardwoods and gymnosperm for softwoods. Examples of hardwoods include beech, mahogany, maple, and teak, while softwoods are cedar, pine, juniper, and spruce. Non-woody biomass are those of agricultural residues, grass family (Poaceae or Gramineae), and non-woody fibers such as cotton fiber [4, 5].

Apart from using biomass in co-firing with fossil fuels, gasification, and pyrolysis, its use in fermentation technology for liquid and gaseous biofuels production is

also applicable and widely studied. The hemicellulose and cellulose structures (so called holocellulose) in lignocellulosic biomass contain sugar monomers that could be utilized by microorganisms and converted to various biofuels via biological pathways.

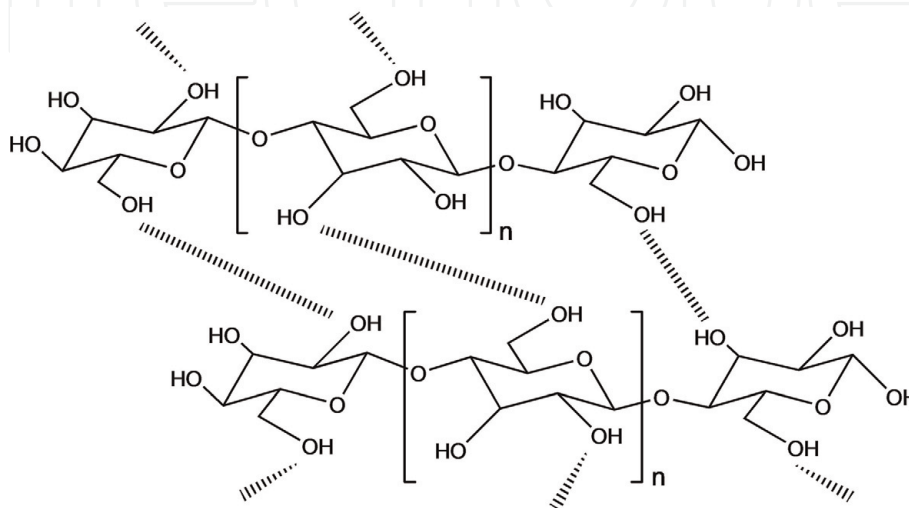
Cellulose is considered a major composition of lignocellulosic biomass. It is a homopolymer containing glucose as the only monomer. Glucose molecules in cellulose are linked by  $\beta$ -1,4-glycosidic bonds (**Figure 1**). Cellulose chain is also known as  $\beta$ -1,4-glucan. The chains are packed into tiny and extremely long structure called microfibrils. These microfibrils are packed into lattices, which make most part of the cellulose fibers inaccessible by enzymes [6–8].

Hemicellulose is also the composition that consists of sugars that can be utilized by microorganisms. It is a heteropolymer of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and uronic acids (4-O-methylglucuronic acid, galacturonic acid). Due to its heterogeneity, different structures of hemicellulose are found in different types of biomass [9, 10].

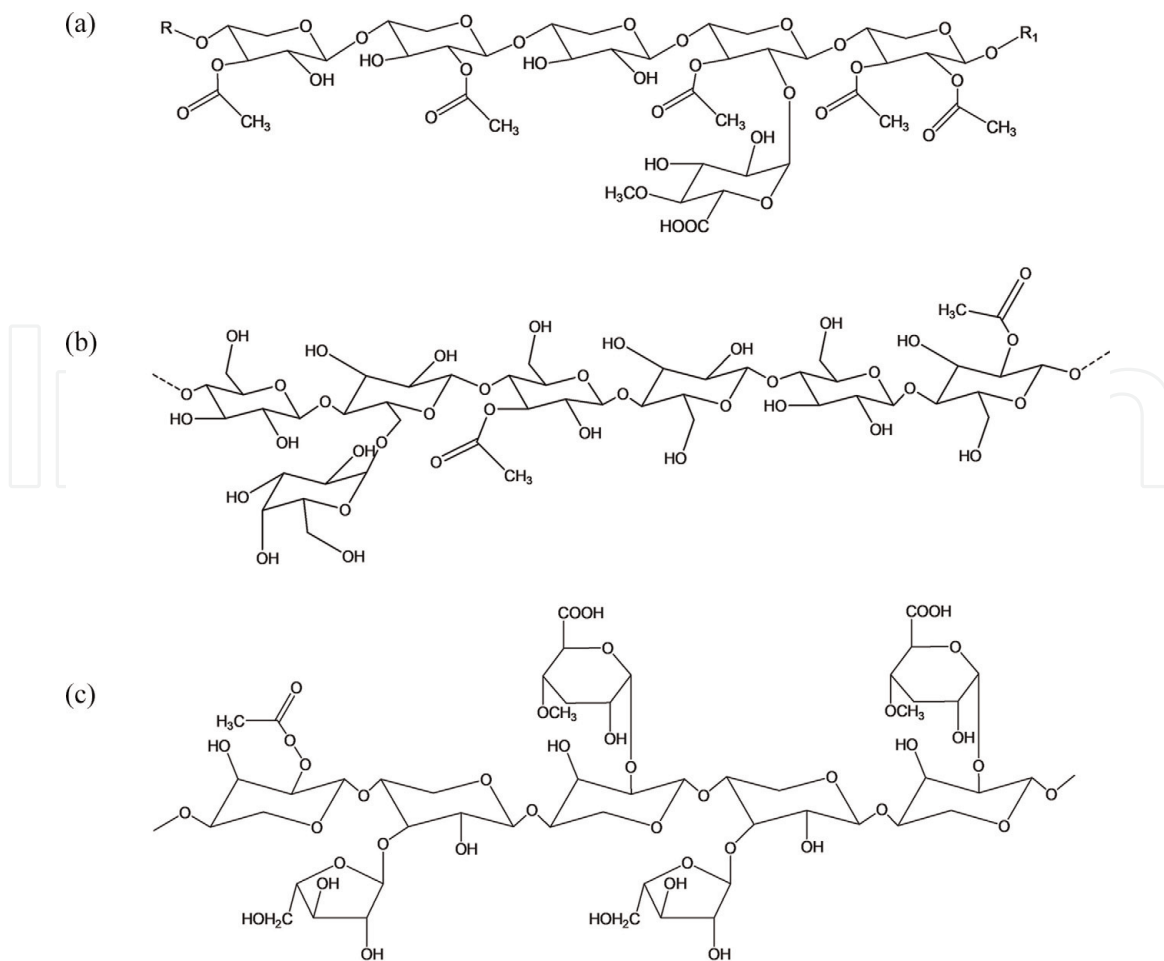
In hardwoods, glucuronoxytan is the major hemicellulose. Its backbone consists of xylose connected by  $\beta$ -1,4-glycosidic linkage, with some acetylation at C2 and C3 of xylose molecules. In addition, side chains of 4-O-methylglucuronic acid are found attached to xylose with  $\alpha$ -1,2-linkage. Main hemicellulose in softwoods is galactoglucomannan. As the name suggests, galactoglucomannan has mannose and glucose as the backbone, with galactose and acetyl group as the side chains. For grasses (including cereals), glucuronoarabinoxylan, wherein xylose is the backbone, is the major hemicellulose [9, 11]. Structures of main hemicellulose in lignocellulosic biomass are illustrated in **Figure 2**.

Some other hemicellulose, which can be found in multiple sources, include xyloglucan which could be found in all hardwoods, softwoods, and grasses, arabinoglucuronoxytan in grasses and softwood. In addition, glucomannan is found as a minor component in softwoods and hardwoods.

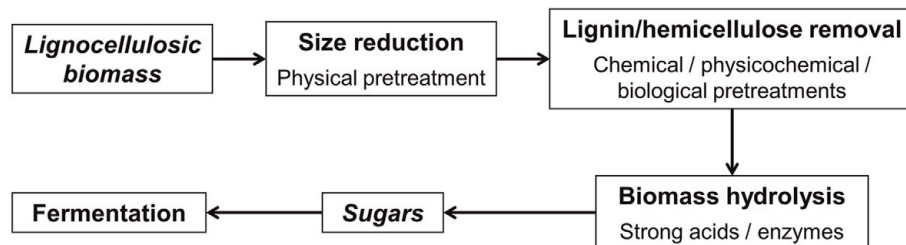
The last major component of lignocellulosic biomass is lignin. Lignin is the only non-sugar component of the biomass. It is the second most abundant biopolymer besides cellulose. It is an amorphous polymer with structures that vary among different types of biomass and environmental conditions. Primarily, lignin consisted of three phenylpropane units of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), which are originated from aromatic alcohols, p-coumaryl, coniferyl, and sinapyl alcohols [12].



**Figure 1.**  
*Structure of cellulose.*



**Figure 2.**  
 Structures of main hemicellulose in hardwoods, soft woods and grasses. (a) Glucuronoxylan, (b) galactoglucomannan, (c) glucuronoarabinoxylan.



**Figure 3.**  
 Basic flow diagram for the use of lignocellulosic biomass in biofuels production through fermentation route.

Although the sugar monomers in holocellulose part of the biomass are of interest for use in biofuel production via biological pathways, breaking down the structure to obtain the monomers is not a simple task. All three components of lignocellulose are incorporated into complex structures and recalcitrant to hydrolysis. Not only the cellulose itself has a strong crystalline structure, its microfibrils are packed and interconnected with hemicellulose. In addition, lignin that fills the void of the structure adds additional strength, increases the hydrophobicity of the wall, and hence prevents the action of hydrolytic enzymes [13, 14].

In order to utilize lignocellulosic biomass in production of biofuels via biological pathways, its tough structures have to be loosen, and hydrolysis of holocellulose needs to be achieved to release sugars for microbial usage. Block diagram in **Figure 3** shows generalized scheme for handling and processing of lignocellulosic biomass when applied in biofuel production by microorganisms through fermentation process.

## **2. Pretreatment of lignocellulosic material**

Lignocellulosic biomass is abundantly available, relatively low-cost, and is a good feedstock for the production of biofuels due to their compositions (cellulose, hemicellulose, and lignin). The natural microorganisms cannot directly ferment lignocellulosic biomass into biofuels. The pretreatment step is required to overcome the recalcitrance attributed to the structural characteristic of lignocellulosic biomass and hydrolyze the lignocellulose biomass into fermentation sugars. Various pretreatment technologies have been proposed, challenging the complexity of biomass structure and attempting to recover high fermentable sugars. The pretreatment methods must meet the following requirements: (1) increase the sugar production or ability to afterward form sugar by enzymatic hydrolysis, (2) minimize the formation of inhibitors that affect the hydrolysis and fermentation process, (3) avoid the loss of carbohydrates, and (4) be cost-effective. The present section summarizes the performance of various pretreatment technologies, including physical, chemical, physicochemical, and biological processes. Furthermore, the advantages and disadvantages of different pretreatment technologies are also included.

### **2.1 Physical pretreatment**

Physical pretreatment involves an increase in the accessible surface area of lignocellulosic materials to enzymes by breaking down the particle size or disrupting their crystalline structures. The physical pretreatment methods such as chipping, milling, and grinding are applied to pretreat several lignocellulosic materials [15]. Chipping and grinding are used to reduce a huge lignocellulosic material into small pieces. Thus, milling is required to mill lignocellulosic material into fine particles. Among these physical methods, milling can significantly reduce the degree of crystallinity and particle size and consequently improve their enzymatic hydrolysis [16]. The energy requirement for physical pretreatment methods depends on the particle size and the reduction of crystallinity in lignocellulosic material. In fact, the required energy is higher than the theoretical energy content available in the biomass [15]. As aforementioned, these methods cannot be used in an industrial scale process due to its cost.

Microwave irradiation is another physical pretreatment method. It is a heating method which directly applies an electromagnetic field to the molecular structure. Microwaves are nonionizing electromagnetic radiation with the wavelengths ranging from 1 mm to 1 m. The electromagnetic spectrums are located between 300 and 300,000 MHz. The application of microwave pretreatment causes swelling and fragmentation of lignocellulosic biomass. The study of Shahzadi et al. [17] indicates that the use of microwave irradiation can enhance the digestibility of lignocellulosic material. In order to enhance the hydrolysis efficiency, microwave pretreatment assisted with catalysts such as acid and alkaline are applied [18]. The advantages and disadvantages of physical pretreatment method are tabulated in **Table 1**.

### **2.2 Chemical pretreatment**

Acid, alkaline, ionic liquid, and organic solvent (organosolv) are used as catalysts in the chemical pretreatment methods. Since 1819, acids including sulfuric and hydrochloric are applied to pretreat lignocellulosic materials [19]. After the discovery, various concentrated and diluted acids have been used to pretreat various lignocellulosic materials [20, 21]. The concentrated acid pretreatments can degrade

Pretreatment method	Effects	Advantages	Disadvantages
Physical			
Chipping, grinding, milling	Reduce the particle size and disrupt the crystallinity	Control of final particle size, easy handling, less water consumption	High energy consumption
Microwave	Swelling and fragmentation of lignocellulosic material	Fast heat transfer, short reaction time, energy-efficient	Low penetration of radiation in bulk products, the distribution of microwave power around of material due to nonhomogeneous material
Chemical			
Acid	Lignin cellulose and hemicellulose fractionate	Enzymatic hydrolysis is sometimes not required as the acid itself may hydrolyze the biomass to fermentable sugars	Corrosive and toxic, formation of inhibitors as by-products
Alkaline	Lignin and hemicellulose removal	Reduce the absorption of cellulose due to efficient lignin removal, low cost	Generates inhibitors, long residence time required
Ionic liquid	Cellulose precipitation and lignin removal	Working under mild reaction condition, low vapor pressure	High cost, complexity of purification and synthesis
Organosolv	Lignin removal and hemicellulose fractionate	Formation of a high purity of lignin	High capital cost, need to separate solvent, need washing step
Physicochemical			
Steam explosion	Particle size reduction, partial hydrolysis of hemicellulose, lignin removal	Less water uses, no chemical uses, low environmental impacts	It has a high equipment cost
Liquid hot water	Partial hydrolysis of hemicellulose, lignin removal	Does not require washing, chemical recovery, or detoxification steps	High water consumption and energy input
AFEX	Decreases the crystallinity and lignin removal	Low formation of by-products	Not suitable for lignocellulosic biomass with high lignin content
SPORL	Lignin removal and hemicellulose fractionate	Low formation of inhibitors, energy-efficient, reduces the absorption by sulfonation of cellulose	High cost of chemical recovery
Biological			
Microorganisms and enzymes	Lignin, hemicellulose, and cellulose degradation	Selective degradation of lignin, hemicellulose, and cellulose, environmentally friendly	Long pretreatment time, the hydrolysis rate is low

**Table 1.** Summary of advantages and disadvantages of each pretreatment methods [22–24].

cellulose and produce a high concentration of inhibitors, such as furfural and 5-hydroxymethylfurfural (5-HMF). In addition, the utilization of concentrated acid causes corrosion of equipment, making the process less attractive [21]. Dilute acid is

an attractive method due to its ability to hydrolyze both hemicellulose and cellulose. As results, pentose sugars (xylose and arabinose) and hexose (glucose) sugar are obtained in the hydrolysate. Moreover, this process minimizes the inhibitor formation compared with concentrated acid pretreatment. However, both concentrated and diluted acids slightly degrade lignin.

Alkaline pretreatment is the most commonly used to degrade lignin in lignocellulosic material. Alkaline reagents, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide (Ca(OH)<sub>2</sub>), aqueous ammonia (NH<sub>4</sub>OH), and oxidative alkaline, are mainly used to cleave the ester linkages in lignin and hemicellulose structures. The cleavages of these linkages significantly enhance the solubilization of lignin and hemicellulose, resulting in a higher cellulose hydrolysis to fermentable sugar by microorganisms or enzymatic hydrolysis.

Ionic liquids (ILs) are salts composed of cations and anions. These liquids have melting point lower than 100°C and low vapor pressure [25]. Anions and cations in ILs form hydrogen bonds with cellulose hydroxyl groups, resulting in a cellulose precipitation. In addition, lignin can be dissolved in the ILs [25]. This reaction occurs in mild conditions with the ease of cellulose recovery, as well as the ILs, with no toxic or odor emission. However, the utilization of ILs to pretreat lignocellulosic materials is not favorable due to its cost. In comparison to other chemical pretreatments, ILs have the advantages of low toxicity, high solvation power, low volatility, thermal stability, as well as inflammability.

In the organosolv process, organic solvents are mainly used to cleave the linkage of lignin and hemicellulose which can increase the pore volume and accessible surface area of cellulose. The resulting lignin is dissolved in the organic solvent phase, while cellulose is recovered as the solid. Many organic solvents such as ethanol, methanol, acetone, organic acids, and ethylene glycol have been utilized to pretreat various lignocellulosic materials. Among these, ethanol is the most favorable solvent due to its low toxicity and its ease of recovery. This process can occur in the presence or absence of catalysts (acid or base) [26]. Comparing with other chemical pretreatments, organosolv process has many advantages such as easy to recover solvent by distillation, low environmental impact, and recovery of high-quality lignin as by-product. Contrastingly, high price of organic solvent and potential hazard of handling large volume of organic solvents limit the utilization of organosolv process. The overall advantages and disadvantages of chemical pretreatments are shown in **Table 1**.

### **2.3 Physicochemical pretreatment**

Physicochemical pretreatment is a combination between physical and chemical pretreatments, which aims to enhance lignin removal and increase the hydrolysis efficiency. Several successful physicochemical pretreatments, such as steam explosion, liquid hot water, wet oxidation, ammonia-based, and sulfite pretreatment (SPORL), are applied to various lignocellulosic materials.

Steam explosion is a combined method between thermo-mechano-chemical treatments. In this process, biomass is exposed to a high pressure (0.69–4.83 MPa) with a saturated steam at a high temperature (160–260°C) for a few seconds [21, 27]. The steam penetrates into the biomass and swells the cell wall of the fibers before the explosion and partial hydrolysis. During pretreatment, the hydrolysis of hemicellulose into hexose and pentose sugars is accomplished by the action of acetic acid produced from the acetyl groups of hemicellulose. This process is called “autohydrolysis.” The efficiency of steam explosion can be enhanced by adding the catalyst such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), SO<sub>2</sub>, or CO<sub>2</sub>. Among these catalysts, acid is the best in terms of sugar recovery, minimization of the inhibition compound

formation, and enzymatic hydrolysis improvement [21]. Liquid hot water pretreatment process is quite similar to steam explosion pretreatment, but it uses water instead of steam. This leads to less formation of inhibitors at the high temperatures.

In the ammonia-based or ammonia fiber explosion (AFEX) process, the lignocellulosic biomass is subjected to liquid ammonia at a high pressure (250–300 psi) and a temperature around 60–100°C for a few minutes. After that, the pressure is immediately released [28]. Liquid ammonia can cause the swelling of lignocellulose structure, resulting in an increase in the enzymatic hydrolysis efficiency. The immediate release of the pressure causes the physical disruption in the crystalline cellulose, resulting in a decrease in the crystallinity of lignocellulosic biomass. However, the lignin and hemicellulose degradation efficiency is low. AFEX process has advantages such as mild reaction temperature and low formation of inhibitors.

SPORL pretreatment process consists of two steps. First, the lignocellulosic materials are treated with magnesium sulfite or calcium sulfite in order to remove the lignin and hemicellulose fractions. Second, the mechanical disk miller is used to reduce the particle size of pretreated lignocellulosic material. This method is efficient to pretreat various lignocellulosic materials [21]. The amounts of HMF and furfural generated from SPORL pretreatment are less than those obtained using acid pretreatment. This is attributed to the fact that at the same acid charge, higher amount of bisulfite leads to higher pH which reduces the decomposition of sugar to HMF and furfural [21].

## 2.4 Biological pretreatment

In the biological pretreatment, microorganisms and enzymes are the key points used to pretreat lignocellulosic materials before enzymatic hydrolysis [22, 28]. Main biological process is delignification and saccharification process. Microorganisms, such as brown, white, and soft rot fungi, have been used to degrade lignocellulosic materials. White and soft rot fungi mainly degrade lignin and hemicellulose while brown rot fungi are used to degrade cellulose [22, 28]. White rot fungi such as *Cyathus stercoreus*, *Phanerochaete chrysosporium*, *Ceriporia lacerata*, *Ceriporiopsis subvermispora*, *Pycnoporus cinnabarinus*, and *Pleurotus ostreatus* are frequently applied to degrade lignin because these species contain lignin degradation enzymes, including peroxidase and laccase [22, 28]. Also, Basidiomycetes species, such as *Bjerkandera adusta*, *Irpex lacteus*, *Fomes fomentarius*, and *Trametes versicolor* are studied for breaking down lignocellulosic materials [11, 12]. Recently, cellulose hydrolyzing bacteria such as Clostridia and Actinomycetes are widely used to pretreat lignocellulosic materials. Clostridia and Actinomycetes grow and degrade lignocellulose under anaerobic and aerobic conditions, respectively [29]. Clostridia have an extracellular complex enzyme system called “cellulosome” that can degrade lignocellulosic materials. This system contains various enzymes, such as endoglucanases, exoglucanases, hemicellulases, chitinases, pectin lyases, and lichenases [30].

As for enzymes used in biological pretreatment, both commercial and extracted enzymes from microbes are used. Commercial cellulase and xylanase are commonly used to degrade lignocellulosic materials such as sugarcane bagasse [31], rice straw [32], napier grass [33], etc. Extracted lignin degradation enzymes, including lignin peroxidase, manganese peroxidase, and laccase, from white rot fungi, are also used to degrade lignin from lignocellulosic materials [28]. The study of Taniguchi et al. [34] found that pretreating rice straw with *Pleurotus ostreatus* enhanced the degradation of lignin and hemicellulose to 41 and 48% degradation efficiency, respectively. The lignin and hemicellulose degradation by *Pleurotus ostreatus* occurs



through the action of peroxidase and laccase. Biological pretreatment is environmentally friendly as no chemicals and lower energy are used compared with other pretreatment methods. The advantages and disadvantages of biological pretreatment methods are given in **Table 1**.

Currently, the combined physical, chemical, and biological pretreatment process is investigated for enhancing the degradation efficiency [21]. The combined process is more effective as compared to a single process. Yu et al. [35] combined physical, chemical, and biological pretreatment process to pretreat rice husk. Results indicate that the combination of chemical (2% H<sub>2</sub>SO<sub>4</sub>) and biological (*P. ostreatus*) pretreatments leads to a higher lignin degradation than single-step pretreatments. The combined pretreatment of napier grass carried out using 2% NaOH along with cellulase enzyme was found to be more effective as compared with single alkaline pretreatment, in which a 3.97 time higher methane production (MP) was obtained [36].

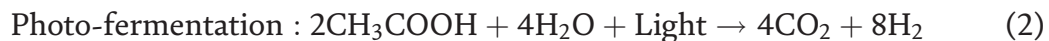
### **3. Potential bio-hydrogen and methane production from lignocellulosic biomass**

Alternative fuels are recently in high demand owing to concerns about depletion of fossil fuels and harmful gases emission problem which results in climate change and environmental deterioration [37]. Biofuels (fuel alcohol, biodiesel/bio-jet, and biogas) can be a suitable alternative to fossil fuels as they are derived from renewable feedstocks, biodegradable, and combusted based on carbon dioxide cycle [38]. Biofuels can be used for the energy generation by combustion or other technologies. They have been used in transportation and power generation sectors, in which the share of biofuel in transport fuel demand has been increasing and reached 3% in 2017 [39]. Biogas (hydrogen and methane) is a highly promising biofuel because it can be produced from a variety of organic feedstocks, including waste biomass which can attribute to the waste reduction simultaneously with energy production [40].

#### **3.1 Hydrogen**

Hydrogen is a noncarbonaceous fuel and energy carrier possessing higher net calorific value compared to other fuels [41]. It can be directly converted into energy in fuel cell or mixed with natural gas for use in internal combustion and jet engines, as well as the gas power turbines. Combustion of hydrogen yields only water; thus it is considered as a clean energy source. The limitation in using hydrogen is its explosivity when mixed with oxygen, leading to difficulty in its storage and distribution [42]. Production of hydrogen from lignocellulosic biomass can be achieved by gasification and microbial fermentation technologies. Gasification is very energy-intensive and releases large amount of carbon, sulfur, and nitrogen oxides to the atmosphere [43]. Therefore, attention had been paid to the microbial fermentation process as it is more environmentally friendly. Bio-hydrogen is a term used to call hydrogen produced via microbial fermentation. Dark- and photo-fermentation are typically applied for bio-hydrogen production. Dark fermentation of organic carbon substrates is carried out by obligate or facultative anaerobic bacteria yielding bio-hydrogen and other side products, such as volatile fatty acids (VFAs) and alcohols. Photo-fermentation requires energy from light to aid the decomposition of organic substrates by photosynthetic bacteria, mostly purple non-sulfur bacteria (PNSB) [44]. The dark fermentative bacteria are capable of utilizing various substrates with high rate of hydrogen production. A drawback of dark fermentation is

its low yield due to the large quantity of side products formed. The substrates for photo-fermentative bacteria are limited to simple sugars and organic acids, and the hydrogen production rate by photo-fermentation is usually lower than dark fermentation [44]. However, with the high substrate conversion efficiency and high hydrogen yield (HY), the photo-fermentation is also considered a promising technology for bio-hydrogen production [45]. In addition, recent research reported the sequential dark-photo-fermentation as an efficient bio-hydrogen production process. The VFAs from dark fermentation are further utilized for hydrogen production in photo-fermentation, thus the HY and substrate conversion efficiency can be improved via sequential dark-photo-fermentation [45–47]. Typical reactions for dark fermentation with acetic acid formation and photo-fermentation can be stated as follows:



Despite the continuing research at the laboratory scale, the biological hydrogen production from lignocellulosic biomass at pilot and industrial scales is still limited. Various kinds of lignocellulosic feedstock have been investigated for bio-hydrogen production by different microorganisms. Typically, the feedstocks are pretreated prior to fermentation in order to enhance hydrogen production efficiency. Pretreatment of the biomass can be conducted by physical (such as size reduction), physicochemical (such as steam, ammonia fiber, and carbon dioxide explosion, hot water, and microwave pretreatment), chemical (such as alkaline, diluted acid, and hydrogen peroxide pretreatment), and biological (such as enzymatic pretreatment) methods. The yield of hydrogen from lignocellulosic feedstocks is diverse depending on the types of substrates, pretreatment methods and microorganisms used. Under mesophilic condition, dark fermentation of untreated water hyacinth by mixed culture of *Enterobacter* sp. and *Clostridium* sp. resulted in 119.6 mL-H<sub>2</sub>/g-VS [48]. Enzymatic hydrolysates of agave bagasse yielded 1.53–3.40 mol-H<sub>2</sub>/mol-substrate by anaerobic mixed cultures [49, 50]. Higher hydrogen production from acid hydrolysate of sugarcane bagasse (6980 mL-H<sub>2</sub>/L-substrate) was observed with mixed cultures compared to the pure culture of *Enterobacter aerogenes* (1000 mL-H<sub>2</sub>/L-substrate) [51, 52].

The pretreated lignocellulosic biomass (in solid form) can also be directly fermented to hydrogen. Alkaline-pretreated sugarcane bagasse fermentation by *C. beijerinckii* yielded 0.733 mmol-H<sub>2</sub>/g-substrate [53]. The HY of 51.9 mL-H<sub>2</sub>/L-substrate was obtained by fermenting corn stover obtained after steam explosion using mixed cultures of *C. celluloblyticum* and *Citrobacter amalonaticus* [54]. The pretreated solid biomass could also be used as feedstocks for hydrogen production via simultaneous saccharification and fermentation (SSF) process. The cellulosytic enzymes mostly perform well under thermophilic condition (50–60°C). However, hydrogen production by SSF under mesophilic condition had been investigated by some researchers based on the optimal temperature for growth and activity of hydrogen producers. Hydrogen yield of 72 mL-H<sub>2</sub>/g-substrate was obtained from acetic acid steam-exploded corn straw by SSF with *Ethanoligenens harbinense* at 37°C [55]. A lower yield of 68 mL-H<sub>2</sub>/g-substrate was obtained from steam-exploded corn straw by SSF with *C. bytyricum* AS1 at 35°C [56].

Fermentation under thermophilic condition (50–65°C) was reported to improve dark fermentative hydrogen production via enhancing substrate degradation rate. Various thermophilic hydrogen producers, such as *Thermoanaerobacterium thermosaccharolyticum* [57, 58], *C. thermosaccharolyticum*, and *C. thermocellum* [59, 60], as well as thermophilic mixed cultures [61], were applied for hydrogen

production from lignocellulosic feedstocks and their hydrolysates. HY of 1947 mL-H<sub>2</sub>/L-substrate from microwave-assisted acid hydrolysate of oil palm trunk (OPT) was achieved using *T. thermosaccharolyticum* KKU19 [62], while the enzymatic hydrolysate of lime-pretreated OPT yielded 2179 mL-H<sub>2</sub>/L-substrate using the same strain [58]. Corn stover hydrolysate obtained by diluted sulfuric acid pretreatment was fermented by *T. thermosaccharolyticum* W16 with a yield of 2.24 mol-H<sub>2</sub>/mol-sugar [63]. When the enzymatic hydrolysate of NaOH-pretreated corn stover was used, the strain W16 produced 108.5 mmol-H<sub>2</sub>/L-substrate [64]. Solid residues of sweet sorghum stalk after hydrogen fermentation was subjected to diluted sulfuric acid hydrolysis. The resulting acid-treated slurry was further fermented by *C. thermosaccharolyticum* DSM572 and yielded 2.5 mmol-H<sub>2</sub>/g-substrate [65]. Activated sludge and anaerobic granular sludge produced 627 and 822 mL-H<sub>2</sub>/L-substrate from diluted sulfuric acid hydrolysate of corn stover under thermophilic condition, which were 2.3 and 3.7 times higher than those obtained under mesophilic condition [61]. Sweet sorghum stalks were used as substrate for hydrogen production by mixed cultures of *C. thermocellum* DSM7072 and *C. thermosaccharolyticum* DSM572. The HY of 5.1 mmol-H<sub>2</sub>/g-substrate was observed [59]. Fermentation of hydrogen by thermophilic microorganisms could overcome the technical challenge of SSF regarding difference between optimal temperatures for enzymatic saccharification and fermentation. SSF of lime-pretreated OPT by *T. thermosaccharolyticum* KKU19 achieved a maximum yield of 60.22 mL-H<sub>2</sub>/g-pretreated OPT [66]. Fungal-pretreated cornstalk yielded 89.3 mL-H<sub>2</sub>/g-substrate by SSF process with *T. thermosaccharolyticum* W16 [67].

Co-digestion with nitrogen-rich organic biomass was reported to enhance hydrogen production from lignocellulosic feedstocks. The OPT hydrolysate co-digested with slaughterhouse wastewater by *T. thermosaccharolyticum* KKU19 gave 2604 mL-H<sub>2</sub>/L-substrate [68]. Co-digestion of napier grass and its silage with cow dung with the bioaugmentation of *C. butyricum* TISTR 1032 yielded 6.98 and 27.71 mL-H<sub>2</sub>/g-volatile solid (VS) [69]. Wheat straw and cheese whey were co-digested by anaerobic granular sludge, and the hydrogen production of 4554, 3685, and 4132 mL-H<sub>2</sub>/L-substrate were observed in 0.11-L serological bottle, 1-L bioreactor, and 4-L bioreactor, respectively [70].

Photo-fermentative hydrogen production mostly uses simple sugars (such as glucose) or organic acids (such as acetic and butyric acids) as substrates. Lignocellulosic hydrolysates with sugar monomers were investigated for hydrogen production. Photo-fermentation of enzymatic hydrolysate of ammonia pretreated wheat straw by *Rhodobacter capsulatus*-PK gave 712 mL-H<sub>2</sub>/L-substrate [71]. Corn stalk pith was hydrolyzed by cellulase enzyme. The resulting hydrolysate was fermented by photosynthetic consortium comprising *R. capsulatus*, *R. sphaeroides*, *Rhodospseudomonas capsulata*, *Rhodospseudomonas palustris*, and *Rhodospirillum rubrum*, in which a HY of 2.6 mol-H<sub>2</sub>/mol-sugar consumed was achieved [72].

Sequential dark-photo-fermentation was applied to increase HY from lignocellulosic biomass. The organic acids obtained from dark fermentation of lignocellulosic biomass are used as substrate for photo-fermentation. The yield of hydrogen from water hyacinth was enhanced from 76.7 to 596.1 mL-H<sub>2</sub>/g-total volatile solid (TVS) by combining dark fermentation (using mixed hydrogen-producing bacteria) with photo-fermentation (using *R. palustris*) [73]. Dark fermentation of pretreated corn stalk by mixed culture from cow dung yield 192.9 mL-H<sub>2</sub>/g-TVS. The yield was increased to 401.5 mL-H<sub>2</sub>/g-TVS by combining with photo-fermentation using *R. sphaeroides* HY01 [74]. Yang et al. [75] reported a HY from pretreated corncob by dark fermentation with mixed cultures from dairy manure of 120.2 mL-H<sub>2</sub>/g-corn cob. Photo-fermentation of the effluent from this process gave 713.6 mL-H<sub>2</sub>/g-COD. The authors also stated that reducing sugars and

oligosaccharides in corncob hydrolysate contributed to the hydrogen produced by dark fermentation, while acetic acid, butyric acid, and alcohols in the dark fermentation effluent contributed to the hydrogen produced by photo-fermentation [75]. A pilot scale test of sequential dark-photo-fermentation from corn stover was investigated. Sewage sludge and photo-hydrogen-producing consortia HAU-M1 were used as inoculum for dark and photo-fermentation, respectively. The overall volumetric hydrogen production rate (HPR) was 7.8 and 4.7 m<sup>3</sup>/m<sup>3</sup>d from dark and photo-fermentation, respectively [47].

### 3.2 Methane

Methane is a fuel gas mainly produced from anaerobic digestion process. Organic substrates are decomposed by diverse microbial communities through a series of metabolic stages during anaerobic digestion, resulting in gaseous products called biogas and inorganic molecules remaining in digestate. Biogas mainly comprises methane (50–75%), carbon dioxide (25–40%), nitrogen (<5%), hydrogen (<1%), oxygen (<1%), and hydrogen sulfide (50–5000 ppm) [76]. Biogas is suitable for use in internal combustion engines and gas turbine generators. Methane has higher octane rating than gasoline, and its combustion produces less CO<sub>2</sub> as compared to fossil fuels [77].

Methane production by anaerobic digestion process involved multiple steps performed by several groups of microorganisms. Typically, anaerobic digestion is divided into four steps that are hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In hydrolysis step, complex organic matters (such as cellulose and protein) are converted into simpler and soluble molecules (such as sugars and amino acids) by hydrolase enzymes excreted by facultative and strictly anaerobic microorganisms called fermentative bacteria. The soluble molecules produced by the hydrolysis steps are then utilized by acidogenic bacteria to produce short-chain organic acids (such as acetic, butyric, and propionic acids) along with hydrogen, carbon dioxide, and alcohols in the acidogenesis step. These products are further consumed in the acetogenesis step to produce acetic acid by acetogenic bacteria. In the last step, acetic acid, hydrogen with carbon dioxide, formic acids, and alcohols were utilized by methanogenic bacteria to produce methane under obligate anaerobic condition [76]. The optimal condition for methanogenic bacteria and other groups of bacteria are different. Some researchers, therefore, introduced two-stage hydrogen and methane production carried out by separating the fermentation into two phases of acidogenesis and methanogenesis, which can promote the methane fermentation rate and increase energy yield from feedstocks [27, 58].

Methane production from various lignocellulosic biomasses has been investigated by different research groups. Due to their complex structures which limit the bioavailability, hydrolysis was reported as the rate-limiting step for methane production from lignocellulosic feedstocks [78]. In order to increase methane production rate (MPR) and improve methane production efficiency, different pretreatment methods such as size reduction, thermal, hydrothermal, alkaline, dilute acid, thermal alkaline/dilute acid, and fungal pretreatments were applied [79–82]. Alkaline pretreatment and combination of alkaline with other pretreatment methods are usually employed, while the thermal pretreatment is reported as the suitable method resulting in greater than 50% increased methane yield compared to un-pretreated feedstocks [83].

Theoretically, the yield of methane, at standard temperature and pressure, from cellulose and hemicellulose are 415 and 424 mL-CH<sub>4</sub>/g with 50% methane content in the biogas [76]. Since the compositions of lignocellulosic biomass are diverse, the yield of methane varies depending on the type lignocellulosic feedstocks used.

Herbaceous biomasses are common lignocellulosic feedstocks for methane production. Corn stover yielded 320–335 mL-CH<sub>4</sub>/g-VS [79, 84]. Co-digestion of corn stover with goose manure increased the methane yield (MY) to 393 mL-CH<sub>4</sub>/g-VS [85]. The straws of wheat, rice, and corn gave 240–329 mL-CH<sub>4</sub>/g-VS [86–91]. Relatively low values HY were observed from biomass of grasses (142–301 mL-CH<sub>4</sub>/g-VS) [36, 83, 92, 93] and woody biomass (136–205 mL-CH<sub>4</sub>/g-TS) [79, 94], while bagasse feedstocks yielded relatively high values of 330–420 mL-CH<sub>4</sub>/g-VS [95, 96].

Two-stage hydrogen and methane production was reported as a successful process to produce hydrogen together with methane and enhance energy recovery from lignocellulosic biomass. Energy yield from OPT hydrolysate increased from 0.8 to 10.6 kJ/g-COD by applying two-stage thermophilic hydrogen and mesophilic methane production in comparison to one-stage thermophilic hydrogen production [57]. The HY of 53.8 mL-H<sub>2</sub>/g-VS together with HY of 133.9 mL-CH<sub>4</sub>/g-VS was achieved by two-stage fermentation of maize silage [97]. Sequential hydrogen and methane fermentation of sugarcane bagasse hydrolysate obtained by steam explosion yielded a total energy of 304.11 kJ/L-substrate [78]. The gaseous (hydrogen and methane) recovery from mixed sugarcane bagasse hydrolysate and water hyacinth was maximized by continuous two-stage hydrogen and methane production at a hydraulic retention time of 8 h and 10 days, respectively, providing energy yield of 8.97 KJ/g-COD [98]. Continuous two-stage hydrogen and methane production from agave bagasse enzymatic hydrolysate was optimized at an organic loading rate of 44 g-COD/L-d (for hydrogen) and 20 g-COD/L-d (for methane), in which 9.22 kJ/g-bagasse was recovered [99].

## 4. Factors affecting dark fermentative hydrogen production

### 4.1 Types of inoculum

Pure and mixed cultures are two types of inoculum used to produce hydrogen by dark fermentation. *Clostridium* sp. and *Enterobacter* sp. are the pure culture widely used to produce hydrogen. Pure cultures give the high HPR and HY [100]. The major disadvantage of using pure culture is the sterile conditions which are required during the start-up and operations resulting in high operation costs from an energy use. This problem can be mitigated by using mixed cultures. Using mixed cultures as an inoculum in bio-hydrogen fermentation process is more practical than those using pure culture because it is simpler to operate, the process is easier to be controlled [101], and its feasibility to use complex organic wastes [100]. Inoculum sources for mixed cultures are animal dung, anaerobic sludge, municipal solid waste, soil, and compost [102]. The presence of hydrogen consumers such as methanogens and homoacetogens is the drawbacks of using mixed cultures. In order to inhibit these hydrogen consumers while harvesting the hydrogen producers, the pretreatment methods including heat treatment; acid treatment; alkali treatment; sonication; aeration; freezing and thawing; addition of specific chemical compounds, e.g., 2-bromoethanesulfonic acid; and addition of long-chain fatty acids are needed [103, 104].

### 4.2 Feedstocks

Various kinds of feedstock have been used to produce hydrogen by dark fermentation. They can be classified into three generations. First-generation feedstocks are food crops such as sugarcane, sugar beet, corn, and cassava which can be

easily digested by fermentative microorganisms. However, there is the concern on food competition and arable land when food crops are used to produce biofuels [105]. Thus, lignocellulosic biomass is developed as the second-generation feedstocks. Due to its compositions, lignocellulosic biomass is difficult to be digested by microorganisms. Therefore, the pretreatment and hydrolysis of the lignocellulosic biomass are needed in order to obtain its underlying monosugars prior the fermentation. Recently, the third-generation feedstock, i.e., microalgae has received high attention to produce hydrogen. Microalgae have rapid growth rate with a high capturing ability for CO<sub>2</sub> and other greenhouse gases. They can be cultivated without soil and have a very short harvesting cycle (1–10 days) [106, 107]. Microalgae biomass consists of high carbohydrates (cellulose and starch) and lipid contents that can be converted to hydrogen by hydrogen producers. HY, HPR, and the overall economy of the process [102] are affected by the differences in carbohydrate content, bioavailability, and biodegradation rate of the first-, second-, and third-generation feedstocks. In addition, the concentrations of feedstocks must be considered because a feedstock or product inhibition can occur in the fermentation process [108].

### 4.3 Nitrogen and phosphate

Nitrogen is required for growth of hydrogen-producing bacteria. Nitrogen source for fermentative hydrogen production is classified into inorganic and organic. Examples of inorganic nitrogen are ammonia nitrogen [109], ammonium bicarbonate [110], and ammonium chloride [111, 112]. Ammonia nitrogen is the most widely used inorganic nitrogen with its optimal concentration in the range 0.1 to 7.0 g/L [113, 114]. Peptone, yeast extract, and corn steep liquor are the examples of organic nitrogen. Ferchichi et al. [115] and Ueno et al. [116] reported that a higher HY was obtained when organic nitrogen is supplied to the fermentation medium.

In fermentative hydrogen production, phosphate is needed due to its nutritious value as well as buffering capacity. An increase in phosphate concentration results in increase of the capability of the bacteria to produce hydrogen. However, too high concentrations of phosphate could cause the substrate inhibition [113, 117]. The optimum C/N and C/P ratios are 74:200 and 599:1000, respectively [118, 119].

### 4.4 Temperature

Temperature affects the maximum specific growth rate, substrate utilization rate, hydrolysis of the substrate, mass transfer rate, hydrogen partial pressure, hydrogenase activity, and the metabolic pathway of the bacteria resulting in a shift of by-product compositions [101, 120, 121]. Fermentative hydrogen production can be operated under a wide range of temperature, i.e., mesophilic (25–40°C), thermophilic (40–65°C), or hyperthermophilic (>80°C) ranges [122]. Thermophilic condition gave a higher hydrogen production than the mesophilic condition. Sotelo-Navarro et al. [123] reported that the bio-hydrogen production from disposable diapers at 55°C was greater at 35°C. This could be due to the increased pace of microbial metabolism in the thermophilic condition. The optimal temperature for fermentative hydrogen production varies depending on the inoculum and substrate types.

### 4.5 pH

pH affects the activity of hydrogenase as well as the metabolism pathway of the microorganisms [109]. Low pH inhibited hydrogenase activity [124, 125] resulting in longer lag time [126] and the inhibition of dark fermentation process. This can be

attributed to the protonation of undissociated acids in medium which can penetrate the microbial cell membrane and inhibit the growth and activities of microorganism [127]. Acidic pH of 4.5–6.0 favors the acetic and butyric acid production pathway. High initial pH leads to the production of ethanol and propionate rather than hydrogen production [128]. The propionate production pathways consume reducing powers that are potentially used for hydrogen synthesis [108].

#### **4.6 Metal ion**

Fe, Ni, and Mg are required for bio-hydrogen production process. These metals are cofactors for enzymes facilitating transport processes in the microorganisms [122, 129, 130].  $\text{Fe}^{2+}$  is an important element to form hydrogenase and other enzymes. Fe-S affects protein functions by acting as an electron carrier and involving in oxidation of pyruvate to acetyl-CoA,  $\text{CO}_2$ , and  $\text{H}_2$  [122]. Additionally,  $\text{Fe}^{2+}$  induces metabolic alteration and is involved in Fe-S and non-Fe-S protein operation in hydrogenase [122, 131]. Nickel is a fundamental component of [NiFe]-hydrogenase. It has the influences on the activity of [NiFe]-hydrogenase. High concentration of nickel inhibits the activity of [NiFe]-hydrogenase, promoting fermentative hydrogen production [122, 132].  $\text{Mg}^{2+}$  is an element that is found abundantly in microbial cells. It stabilizes ribosomes, cell membranes, and nucleic acids and plays a crucial role as an activator of many kinases and synthetases [133]. Cu, Cr, and Zn also have influences on hydrogen fermentation process [122]. The relative toxicity of these heavy metals are Zn (most toxic) > Cu > Cr (least toxic).

#### **4.7 Hydraulic retention time**

Hydraulic retention time (HRT) is defined as the time that fermentation broth remains in a reactor. It is related to the working volume of the reactor and the influent flow rate. HRT affects a continuous hydrogen production. Hydrogen-producing bacteria are fast-growing bacteria, so they prefer short HRT, while the methanogens are slow-growing microorganisms, so they prefer long HRT [134]. Therefore, HRT can be used as controlling parameters to suppress the community of methanogens [102]. Jung et al. [134] reported that the HRT for treating liquid-type substrate is shorter than that of solid-type substrate because the times to hydrolyze substrate containing high solid are much longer.

#### **4.8 Hydrogen partial pressure**

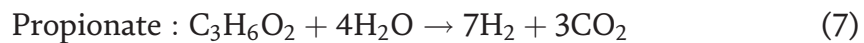
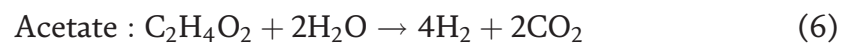
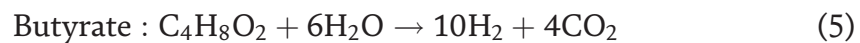
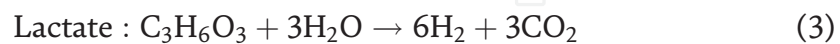
Hydrogen partial pressure affects hydrogenase activity because it is involved in reversibly oxidizing and reducing ferredoxin [102]. High accumulation of hydrogen partial pressure in the fermentation broth decreases the hydrogen production because the reaction tends to be reducing ferredoxin rather than oxidizing ferredoxin [135]. Hydrogen partial pressure can be reduced by biogas sparging [136], agitation, and reduction of headspace pressure using vacuum pump or enlarging the headspace volume.

### **5. Factors affecting photo-fermentative hydrogen production**

#### **5.1 Carbon sources**

Various kinds of substrates can be used as carbon source by PNSB. Short-chain organic acids such as malic, lactic, succinic, acetic, propionic, and butyric acids

[137–141] are the most generally used substrates for photo-hydrogen production. VFAs in the hydrogenic effluent can also be used to produce hydrogen by PNSB [142–145]. Additionally, other carbohydrate substrates [37, 146, 147] and organic acids from industrial wastewaters can be utilized as carbon source by PNSB [148–151]. Carbon affects the metabolism of cell growth and photo-hydrogen fermentation system [152, 153]. Cell formation utilizes large fraction of carbon, while hydrogen production utilizes a smaller fraction. The efficiency of photo-hydrogen production is different according to the types of carbon substrates. This is due to the variations in the electron transfer capabilities in the different metabolic pathways of photosynthetic microbes [154]. Substrate concentration can also affect the photo-hydrogen production. The optimum concentrations of VFAs for photo-hydrogen production were reported in the range of 1800–2500 mg/L [155, 156]. The maximum theoretical HY from different carbon substrates are as follows:



## 5.2 Nitrogen sources

Nitrogen is an essential nutrient for cell synthesis and hydrogen production. The activity of nitrogenase, an enzyme involved in the hydrogen production by photosynthetic bacteria, is greatly affected by nitrogen. Glutamate is a preferred nitrogen source for PNSB. It was rapidly consumed and could also improve hydrogen production of photo-hydrogen-producing bacteria [157–159]. Ammonia has an adverse effect on hydrogen production. High concentration of ammonium ions powerfully inhibited the synthesis and activity of nitrogenase. However, a low ammonium concentration less than a non-inhibitory level can support the growth of cells and is able to enhance the photo-hydrogen production.

## 5.3 pH

pH affects the ionic concentration in the medium. These ionic forms influence the active site of nitrogenase and affect the biochemical characteristic in microbial cells during metabolism process [154, 160]. Optimal pH for photo-hydrogen production of PNSB was 7.0 [140, 161–164].

## 5.4 Temperature

An increase in the environmental temperature until the optimal temperature can improve the activities of the nitrogenase and proteins associated with the cell growth or hydrogen production. An imbalance of incubation temperature on cells growth inhibits the physiological activity, intracellular enzyme activity, and metabolism of cells. Unstable temperature may cause bacteria to spend their energy for adaptation to low/high temperatures in order to be able to survive [165] which results in a reduction in the hydrogen production, HPR, HY, and substrate conversion efficiency [139, 154, 166].



## 5.5 Light energy

Light energy is a necessary resource for the reaction, electron transport, ATP synthesis, and hydrogen production [165, 167]. Light intensity influences the HPR and cell synthesis [160, 163, 168]. At the optimal light intensity, large amounts of ATP and reductive power are sufficient for nitrogenase activity to produce hydrogen and generate the cells. However, a further increase in light intensity greater than the saturation condition became an inhibitory for hydrogen production by PNSB. Photo inhibition occurs when the photosynthetic system supplies excess ATP and  $Fd_{red}$  in comparison to the capacity of nitrogenase enzyme [169]. Consequently, the cell is damaged by the bleaching bacteriochlorophyll pigment during the extra-light cultivation [170].

Halogen [141, 152, 171], tungsten [155, 161], fluorescent [172], infrared [172], and light-emitting diode (LED) lamps [173, 174] have been used as the light source for photo-hydrogen fermentation. Among these lamps, LED has the high operational stability and can improve the performance of photo-hydrogen fermentation [154]. Other advantages of LED include specific wavelengths (770–920 nm), lower electricity consumption, lower heat generation, and longer life expectancy [154, 174].

## 5.6 Iron concentration

Iron is the major cofactor at the active site of FeMo-nitrogenase [157, 175]. There are 24 atoms of Fe as the composition in each molecule of nitrogenase [176]. It is also an essential component in ferredoxin and cytochrome b-c complex, which are electron carriers of the photosynthetic electron transport system. Ferredoxin also contains  $Fe_4S_4$  in a cluster of nitrogenase [177]. Photo-hydrogen production is functioned by nitrogenase, which receives electron carriers from ferredoxin and reduces protons to molecular hydrogen. The optimal  $Fe^{2+}$  concentration for photo-hydrogen fermentation are in the range of 1.68–35 mg/L [164, 177–179]. Concentration of iron greater than the requirement of regular physiological metabolisms can disrupt the cell surface of microorganisms. As a consequence, the production of hydrogen is reduced [177].

## 5.7 Vitamin solution

Vitamins are essential for carbohydrate, protein, lipid, and cell metabolism [180, 181]. Vitamin B1 (thiamine) is a precursor of thiamine pyrophosphate (TPP), a coenzyme of the pyruvate dehydrogenase complex, essential for catabolism of carbohydrates, organic acids, and amino acids. This is important in the conversion of pyruvic acid and provides acetyl-CoA in the TCA cycle which supports cell synthesis. Biotin is a part of an enzymatic carboxylation and is a cofactor for carbon dioxide fixing enzymes such as pyruvate carboxylase. Oxaloacetate is supplied by pyruvate carboxylase. This is important in the citric acid cycle and in the production of biochemical energy. Vitamin B6 (pyridoxamine) is necessary for the metabolism of amino acid and in glycogen hydrolysis [181–183]. Nicotinic acid is a precursor of  $NAD^+$ / $NADP$ , which are electron carrier and play an important role in electron transfer during the photo-fermentation process [180].

## 5.8 Inoculum concentration

The ratio of initial cell concentration ( $X_0$ ) to initial substrate concentration ( $S_0$ ) affects the initial energy level of microorganisms. This energy is necessary to

support the cell synthesis and metabolism process [140]. At a high  $S_0/X_0$  ratio, i.e., low seed inoculation, microorganisms require more adaptation to utilize the high substrate concentration leading to a delay of the lag period for photo-hydrogen fermentation [140, 162, 163]. A further increase in cell concentration to greater than the optimal level resulted in a decreased hydrogen production [140, 162, 163]. A low  $S_0/X_0$  ratio, i.e., high seed inoculation, resulted in an insufficiency of the substrate to supply the growth of cells [140]. In addition, excess biomass prevents penetration of light into the cultivation system due to a self-shading effect. This leads to a decrease in light intensity that causes a reduction of ATP creation resulting in the decrease of hydrogen production by photosynthetic bacteria. Moreover, extracellular concentrations might promote the formation of bacterial flocs or biofilm creation which can limit substrate distribution inside the bioreactor system [140, 157, 167].

## 6. Factors affecting methane production

### 6.1 pH

pH influences the growth of microorganisms in various stages of the anaerobic digestion (AD) process [184, 185]. Optimum pH for methanogens to produce methane ranges from 7.0 to 7.2 [186]. pH outside the range of 6.0–8.5 is toxic to methanogens. pH values below 6.6 starts to adversely affect the activities of the methanogens, and the values below 6.2 are significantly toxic to the methanogens. During the acidogenesis stage of AD process, the pH in an anaerobic digester decreases to below 6.0 due to VFAs accumulation and carbon dioxide production. After this, the pH rises to 7.0–8.0 or above. Yu and Fang [186] and Kim et al. [187] found that the optimal hydrolysis and acidogenesis stage were achieved at pH 5.5–6.5, and the acidogenic bacteria continue to produce the acids until the pH drops to 4.5–5.0 [186, 188, 189]. As a consequence, the activity of methanogens is inhibited. Thus, it is recommended that the hydrolysis, acidification, acetogenesis/methanogenesis stage in AD process should be carried out separately [190].

### 6.2 Temperature

Most of the methanogens are mesophile which are active in the temperature ranges of 30–35°C, while only a few are thermophile which are active in the temperature ranges of 50–60°C [186]. Deublein and Steinhauser [190] reported that the methanogenic activity is inhibited at the temperatures between 40 and 50°C especially at the values near 42°C. This is believed to be a transition temperature from mesophilic to thermophilic temperature [191].

### 6.3 Hydraulic retention time

HRT affects the rate and extent of methane production. A long HRT results in higher total VS mass reduction, which in turn leads to higher cumulative biogas production as well as to allow the microorganisms to acclimate to toxic compounds [191]. Methanogens have a long generation time. Thus, the HRT is usually set at 10–15 days to avoid the washout from the reactor [186]. The length of HRT can vary depending on bacterial strains, operation condition, and so on.

## **6.4 Substrate composition**

Biogas yield and the compositions of biogas are greatly influenced by the composition of feedstocks. AD of carbohydrates, fats, and protein yield 886, 1535, and 587 L biogas/kg-VS with methane content of approximately 50, 70, and 84%, respectively, [184]. Substrate to inoculum ratio (S/I), as well as biodegradability of the substrate, is another important factor affecting batch AD processes, especially at high solid content [192]. Too high S/I ratio may be toxic, while too low S/I ratio may prevent induction of the enzyme necessary for biodegradation [193]. Too high concentration of feedstock can cause inhibition or failure of AD [194] due to substrate inhibition. High S/I ratio can lead to overloads due to VFAs accumulation [192, 195] and long lag phase. Thus, a low S/I ratio is preferred in order to attain shorter lag phase [192, 196]. Owen et al. [197] proposed a standard S/I ratio to be approximately  $1 \text{ g-VS}_{\text{substrate}}/\text{g-VS}_{\text{inoculum}}$ .

## **6.5 Organic loading rate**

Organic loading rate (OLR) is defined as the amount of VS or COD components fed per day per unit digester volume. Higher OLR can reduce the digester's size and the capital cost as a consequence. However, enough time (HRT) should be provided to the microorganisms for breaking down the organic material and converting it into gas [198]. An increase in OLR can result in higher hydrogen production efficiency [199]. However, a further increase in OLR beyond a certain level will result in substrate inhibition, leading to a lower MY [200]. Too high OLR can shift the metabolic to solventogenic phase [201]. Hobson and Bousfield [201] and Chandra et al. [185] reported that a total solid content of 8.0–10.0% is desirable for optimum MY.

## **6.6 Alkalinity**

Buffer capacity, or alkalinity in AD process, is the equilibrium of carbon dioxide and bicarbonate ions that provides resistance to significant and rapid changes in pH. Alkalinity is proportional to the concentration of bicarbonate. The imbalance of digester can be more reliably measured by a buffer capacity than a direct measurement of pH. This is because an accumulation of short-chain fatty acids will reduce the buffering capacity significantly before the pH decreases. A low buffer capacity can be improved by reducing OLR. This is because too high OLR inhibited the microorganisms due to too high fatty acid concentration. Reducing OLR therefore reduces the availability of these fatty acids. Then, the alkalinity of the system can be improved. Guwy et al. [202] and Ward et al. [189] indicated that a quicker way is to add strong bases or carbonate salts to remove carbon dioxide from the gas space and convert it to bicarbonate. Alternatively, bicarbonate ( $\text{HCO}_3^-$ ) can be added directly.

## **6.7 Carbon to nitrogen (C/N) ratio**

C/N ratio is a ratio of the mass of carbon to the mass of nitrogen in a substance. In AD process, a C/N ratio ranging from 20 to 30 is considered optimum [184, 185], and the value of at least 25:1 is suggested for optimal gas production [191]. If the C/N ratio is too high, methanogens will rapidly consume the nitrogen to meet their protein requirements and will no longer react with the rest of carbon in the material. As a result, gas production will be low. On the other hand, if the C/N ratio is too low, nitrogen will be liberated and accumulated in the system in the form of

ammonium ion ( $\text{NH}_4^+$ ). This can possibly increase the pH of the digestate to a level that is toxic to methanogens (pH 8.5) [186, 203].

## 7. Processes for bio-hydrogen and methane production from lignocellulosic materials

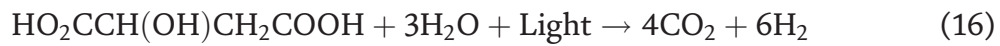
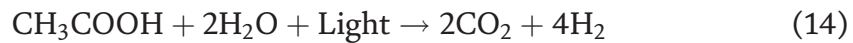
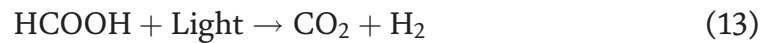
The abundance of lignocellulosic biomass makes it a viable feedstock for hydrogen ( $\text{H}_2$ ) and methane ( $\text{CH}_4$ ) production. Cellulose in lignocellulosic biomass can be saccharified to glucose then fermented to hydrogen and methane. In this section, summarized details on fermentative conversion process for hydrogen, i.e., dark fermentation and photo-fermentation, methane production, and AD are given.

### 7.1 Processes for fermentative hydrogen production

The methods that are investigated widely for fermentative hydrogen production are dark fermentation, photo-fermentation, and a coupling system comprising dark fermentation and photo-fermentation [204]. Dark fermentation is an acidogenic fermentation process conducted under anaerobic conditions in the absence of light. Dark fermentation, as compared to photo-fermentation, is regarded as a more promising method [42], owing to its ability to utilize a wide range of biomass, its high hydrogen production rate, and its independence of lighting conditions [109]. Microorganisms used in dark fermentation are strictly anaerobic bacteria, particularly those in the genus *Clostridium*, and facultative anaerobic bacteria, e.g., *Enterobacter* spp. [205]. Mixed cultures, for example, sludge compost and sewage sludge, are also used [204]. In theory, the maximum HY obtained under dark fermentation is 4 mol- $\text{H}_2$ /mol-glucose when acetic acid is produced as a co-product (Eq. (9)). This is roughly equivalent to one third of energy recovery from the biomass [204]. The HY of 2 mol- $\text{H}_2$ /mol-glucose can also be obtained when butyric acid is produced as the co-product (Eq. (10)). However, when mixed culture is used, mixed acids are often produced, leading to a lower HY of 2.5 mol- $\text{H}_2$ /mol-glucose (Eq. (11)).



Photo-fermentation is another process being investigated widely for hydrogen production from biomass. Unlike dark fermentation, photo-fermentation is a process that requires light to drive the conversion of organic substrates into hydrogen. Purple non-sulfur bacteria are a group of microorganisms responsible for hydrogen production under photo-fermentation. Examples of PNSB include *Rhodobacter* spp., *Rhodospseudomonas* spp., and *Rhodospirillum* sp. Photo-fermentation is a process known for its high substrate conversion efficiencies [206]. In theory, photo-fermentation can completely convert organic compound into hydrogen, i.e., 12 moles of hydrogen can be obtained from a mole of glucose (Eq. (12)), which is much higher than that obtained through dark fermentation (4 mol- $\text{H}_2$ /mol-glucose). However, when VFAs are used as the substrate, lower HYs in a range 1–10 mol- $\text{H}_2$ /mol-VFA are obtained (Eqs. (13)–(17)). In photo-fermentation, it was reported that PNSB showed an affinity toward VFAs, with malate and lactate being the most preferable substrate. Nevertheless, a good yield is also reported using acetate as the substrate [206].



Due to the ability of photo-fermentation to utilize VFAs as the substrate for hydrogen production, in recent years, much attention has been paid on improvement of hydrogen production from biomass using coupling systems comprising dark fermentation and photo-fermentation. Anaerobic bacteria and PNSB can be co-cultivated in a single bioreactor, so that VFAs produced as the co-products during dark fermentation are instantly converted into hydrogen by photo-fermentation. Several co-cultivation of anaerobic bacteria, either pure or mixed culture, and PNSB have been reported in literatures with better HYs compared with the use of single-strain cultivation, for example, *C. butyricum* and *Rhodobacter* sp. M-19 [207], *C. butyricum* and *R. sphaeroides* [208], and *Lactobacillus delbrueckii* and *R. sphaeroides* RV [209], and heterotrophic consortium and *R. sphaeroides* N7 [210]. However, the implementation of this integrated dark fermentation-photo-fermentation system is still hindered by the great differences in growth rate and acid tolerance between anaerobic bacteria and PNSB [211].

Alternatively, dark fermentation and photo-fermentation can be performed sequentially in separated reactors. In this process configuration, dark fermentation effluent containing VFAs is fed, after some adjustments such as dilution and neutralization [204], into photo-fermentation reactor to allow the conversion of VFAs to hydrogen by PNSB. This sequential process is generally easier to operate and control compared with the co-cultivation system as dark fermentation and photo-fermentation are operated separately. Recently, the sequential dark fermentation-photo-fermentation process was tested at a pilot scale using corn stover hydrolysate as a substrate in 11 m<sup>3</sup> reactor (3 m<sup>3</sup> for dark fermentation and 8 m<sup>3</sup> for photo-fermentation). Results showed that 59.7 m<sup>3</sup>/d of hydrogen was produced, of which 22.4 m<sup>3</sup>/d was from dark fermentation and 37.3 m<sup>3</sup>/d was from photo-fermentation [47]. This demonstrates clearly that the sequential dark fermentation-photo-fermentation process is more efficient in conversion of biomass into hydrogen, compared with a single-stage dark fermentation or photo-fermentation process.

## 7.2 Process for methane production

A process for fermentative production of methane is generally called AD. AD is a microbiologically mediated process, in which organic compounds are converted into methane and carbon dioxide in the absence of oxygen [212]. AD process consists of four sequential stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis, and involves several groups of microorganisms. The hydrolysis is a stage that macromolecules (protein, fat, carbohydrate) are degraded to water soluble monomers (amino acids, fatty acids, and sugars). These monomers are then fermented to VFAs (acetic, propionic, lactic, butyric, and valeric acids) during the acidogenesis stage. The fermentation products after acidogenesis are subsequently converted into acetic acid, carbon dioxide, and hydrogen in the acetogenesis stage

before acetic acid and hydrogen are consumed to produce methane [213]. AD process have been used to produce methane from a wide variety of lignocellulosic biomass, e.g., corn stover, barley straw, rice straw, wheat straw, sugarcane bagasse, and yard waste [200, 214]. Biochemical methane potential (BMP) of a selected biomass with a formula  $C_aH_bO_c$  can be estimated using Buswell's equation (Eq. (18)), while Boyle's equation (Eq. (19)) is used to estimate BMP of biomass with a formula  $C_aH_bO_cN_dS_e$ , where a, b, c, d, e is the molar fraction of C, H, O, N, S, respectively. It should be noted that Eqs. (18) and (19) are used assuming the total stoichiometric conversion of organic matter into methane and carbon dioxide [215]. Using cellulose ( $C_6H_{10}O_5$ ) as an example, BMP estimated using Eq. (18) is 415 mL/g-VS:

$$BMP = \frac{\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right)}{(12a + b + 16c)} \times 22,400 \quad (18)$$

$$BMP = \frac{\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)}{(12a + b + 16c + 14d + 32e)} \times 22,400 \quad (19)$$

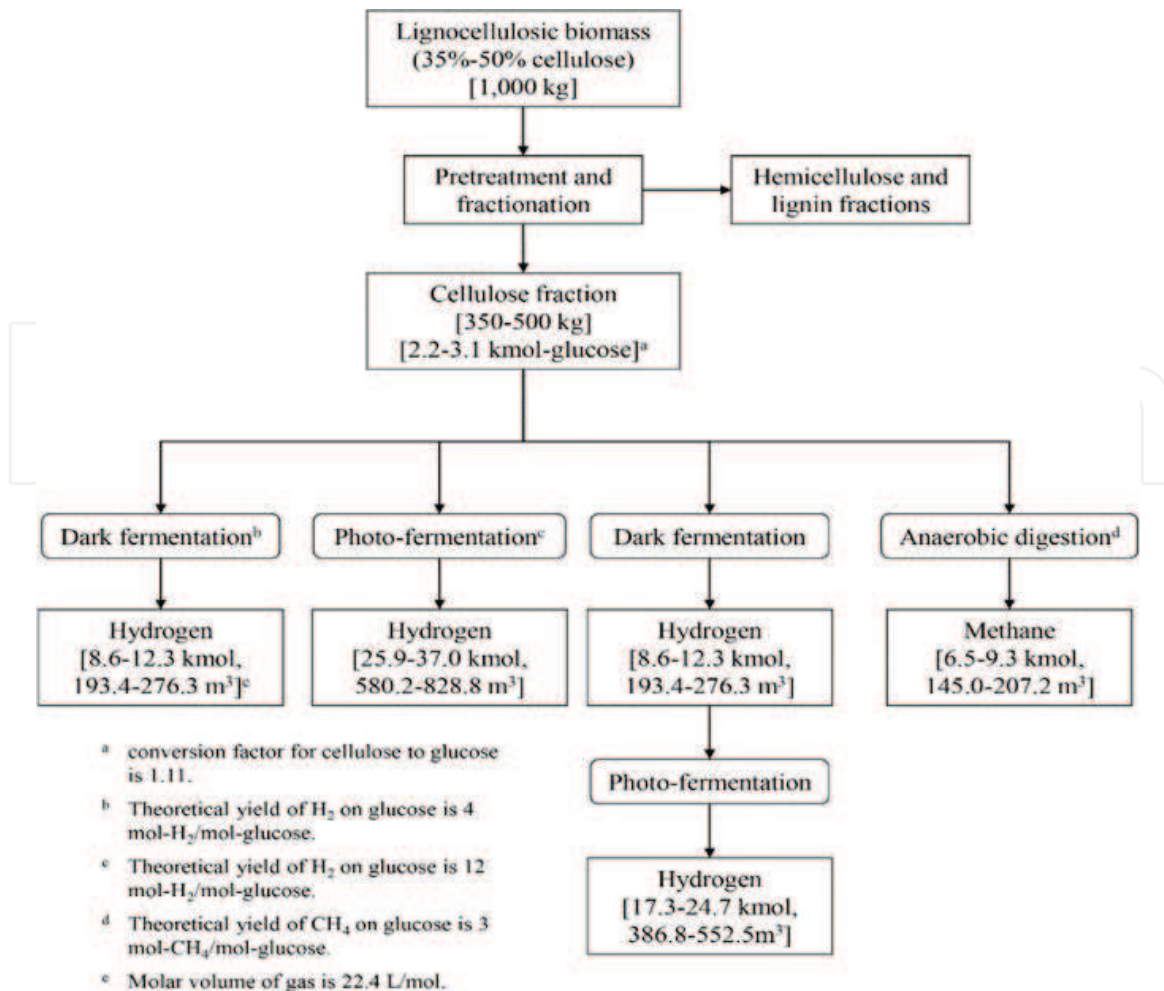
Alternatively, organic fraction composition of biomass can be used to estimate the theoretical methane production using Eq. (20) [216]:

$$BMP = (415 \times \%carbohydrate) + (496 \times \%protein) + (1014 \times \%lipid) \quad (20)$$

AD process can be divided, based on the percentage of total solids (TS) in the system, into liquid-AD (L-AD) and solid-state AD (SS-AD). Although the criteria for this classification is not clear, it is generally accepted that systems containing less than 15% TS are called L-SD and those containing 15% TS or higher are called SS-AD. While L-AD is a traditional process being used extensively for waste treatment, SS-AD is relatively new, being developed in the past decades for municipal solid waste treatment [217]. Comparing between the two, SS-AD has many advantages over L-AD, including a smaller reactor volume, thus higher volumetric productivity of methane, higher organic loading rate, lower water consumption, lower energy input for operation (heating and mixing), and no problems of floating and stratification of fats [218]. However, due to a relatively high TS content of the system, limitation of mass and heat transfers can occur during the process, leading to a low fermentation yield. The use of SS-AD on wheat straw, corn stover, switch grass, and grass silage was reported to produce 55–197 L- $CH_4$ /kg-volatile solids [219], while methane production of 45–290 L/kg-volatile solids were obtained from rice straw, corn straw, wheat straw, and yard waste [200].

## 8. Bioconversion process for lignocellulosic materials to bio-hydrogen and methane

Based on average composition of lignocellulose, 35–50% cellulose, 20–35% hemicellulose, and 10–25% lignin [220], bioconversion processes for cellulose into hydrogen and methane through dark fermentation, photo-fermentation, sequential dark fermentation-photo-fermentation, and AD are presented (**Figure 4**). Starting with 1000 kg of lignocellulosic biomass containing 35–50% cellulose, 193.4–276.3  $m^3$  of hydrogen is obtained by dark fermentation, 580–828.8  $m^3$  of hydrogen is obtained by photo-fermentation and a sequential dark fermentation-photo-fermentation, and 145.0–207.2  $m^3$  of methane is obtained by AD.



**Figure 4.** Theoretical hydrogen and methane yields obtained from dark fermentation, photo-fermentation, sequential dark fermentation-photo-fermentation, and anaerobic digestion for hydrogen and methane production from lignocellulosic biomass.

## 9. Conclusion

Lignocellulosic materials are the promising substrate for bio-hydrogen and methane production. The main compositions of lignocellulosic materials are cellulose, hemicellulose, and lignin. In order to obtain the underlying monosugar, the appropriate pretreatment methods are recommended to hydrolyze hemicellulose or to remove lignin. Physical pretreatment can be used to increase the accessible surface area of lignocellulosic materials prior to the subsequent hydrolysis. Chemical hydrolysis by means of dilute acid pretreatment is an effective method to hydrolyze both hemicellulose and cellulose in lignocellulosic materials. Though, this method can slightly degrade lignin. Lignin can be effectively removed by alkaline pretreatment. Biological pretreatment by microorganisms and enzymes can be used to pretreat the lignocellulosic materials before enzymatic hydrolysis. Combined physical, chemical, and biological pretreatment process is more effective than a sole process. Bio-hydrogen and methane production process is greatly affected by the environmental factors. The ranges of these factors mainly depend on, but not limited to, the types of feedstocks and microorganisms in the process. Dark fermentation followed by photo-fermentation is more efficient in producing hydrogen from lignocellulosic materials than the single-stage fermentation. Methane production from lignocellulosic materials is an environmentally friendly process for producing bioenergy and managing the waste at the same time.

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