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REVIEW ARTICLE

Potential for biohydrogen production from organic wastes with focus on sequential dark- and photofermentation: the Philippine setting

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Abstract

Fossil fuel remains the world's main source of energy, but its massive use leads to the exhaustion of natural energy resources as well as climate change. With this, the interest in developing alternative energy sources has emerged globally—among these is hydrogen. Among the hydrogen production approaches, biological fermentation has been attracting global attention because of its environmental and economic merits. This process utilizes diverse feedstocks including complex organic waste materials. The Philippines has a great potential to produce hydrogen from biomass primarily because it is an agricultural country. The country is abundant in various agricultural wastes such as livestock manure, and plant residues of rice, corn, sugarcane, and coconut, as well as agro-industrial and municipal organic wastes with millions of tons generated per year. A number of studies have explored the use of technologies such as the dark fermentation (DF), photofermentation (PF), and the integration of DF and PF to utilize organic wastes for biohydrogen production. This review paper provides an overview of the organic waste scenario in the Philippines including approaches to utilize different wastes for fermentative biohydrogen production. An initial estimate conducted on the biohydrogen production suggested that the Philippines can yield 0.34–2.24 × 10^6 t/year from agricultural residues alone using the proposed two stage DF-PF hybrid system, with a positive net energy conversion, hence validating the possibility of establishing a biohydrogen production system from organic wastes generated in the country.

Keywords Biohydrogen · Organic waste · Dark fermentation · Photofermentation

1 Introduction

Depleting fossil fuel reserves and myriads of environmental concerns due to the increasing greenhouse gas emissions propelled the research on renewable and sustainable alternative energy sources. Renewable energy could be derived from solar, wind, geothermal, tidal, hydro, and biomass. Among the available renewable energy resources, biofuel is gaining popularity because of its application in the transport sectors. Bioethanol and biodiesel [1], for example, have found market patronage. Combustion of these organic alternative fuels can however contribute to the increasing amount of carbon dioxide in the atmosphere which has been one critical issue concerning global warming. The potential of hydrogen as one emerging alternative energy source lies on the fact that combustion of H_2 produces only water and releases a high amount of energy. Despite being the simplest and the lightest element in the universe, H_2 has the highest specific energy content among all conventional fuels [2] with an energy yield of 120 MJ/kg. This value is approximately 2.75 times higher than hydrocarbon fuels. Apart from providing a technology of zero carbon emission, hydrogen works well with fuel cells and is compatible with existing internal combustion engines. Moreover, it can be transformed to other forms of energy such as heat and electricity, making it one of the most fascinating and versatile energy resources [3].

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Aside from its promising potential in the energy sectors, hydrogen holds various applications as raw material in different manufacturing industries. It is primarily used in the production of fertilizers, synthesis of other chemicals, hydrogenation of hazardous wastes, food preparation, rocket fuel, and petroleum refineries [3, 4].

Majority of the hydrogen used in industries is produced by steam reformation of non-renewable hydrocarbon or coal gasification—processes that bear huge greenhouse gas footprint [5, 6]. Alternatively, hydrogen can be produced by electrolysis, a process that splits water molecules into hydrogen and oxygen. The electrolysis of water, however, is considered the "worst energy-intensive" method of producing hydrogen [3, 7]. At present, efforts are being made to improve the efficiency of electrolyzers by minimizing energy losses during the process. The electrolysis process is being combined with other renewable energy resource to supply the needed energy during the process. Several of those combined processes are the photovoltaic-electrolysis, wind-turbine-electrolysis, and hydropower-electrolysis systems. Although the context of renewable energy utilization is apparently appealing, the electrolysis process is not analogous to the goal of obtaining an ultimate solution in producing hydrogen in efficient and sustainable manner as the electricity consumed during the process is far more costly than the hydrogen produced [7]. A sustainable H_2 production is going to be an essential research endeavor if the global economy is to transition into a hydrogen economy.

Hydrogen can also be produced through biological routes. Several microbial-driven biochemical reactions can form hydrogen from organic materials, or from water using external energy sources such as light. Hydrogen generated from such production processes is called biohydrogen. These biological routes include biophotolysis, microbial electrolysis, and fermentation. Biophotolysis is a water-splitting process by green algae or cyanobacteria. It produces oxygen and hydrogen in the presence of light and water via direct or indirect routes. On the other hand, microbial electrolysis involves the production of hydrogen from organic substrates in a microbial cell by the application of an external electric current [8]. Fermentation, on the other hand, is a process that can be operated in dark or light conditions wherein fermentative bacteria breakdown organic substrates to produce hydrogen along with other by-products, anaerobically. Compared to non-biological hydrogen production processes, biological approaches in general are more ecologically sound, requires less energy, and have the potential to become cost-competitive since these processes utilize low-value biomass wastes as feedstock [1].

2 Philippine organic waste scenario

The Philippines, like other developing countries, holds emerging industrial sectors that yield a substantial amount of solid wastes and wastewater. With the increasing population and economic activities, it is expected that these wastes will continue to rise and create a pollution problem, if not properly managed [9]. A considerable fraction of these wastes are organic substances which include crop residues and animal wastes from agricultural production, agro-industrial wastes, and municipal solid wastes [10]. This paper examines the status of organic waste generation in the Philippines and its potential for biohydrogen production.

2.1 Agricultural wastes

Being an agricultural country, the Philippines produces tons of agricultural residues. Major crops planted in the country are sugarcane, coconut, rice, and corn with an annual production of at least 7 Mt per year [11]. This also generates massive residues from harvesting and processing such as rice straw, rice hulls, corn cobs, sugarcane bagasse, and coconut shells and husks (Table 1). Several traditional practices are able to utilize these residues. For instance, chopped leaves and tops from the sugarcane are left in the fields for mulching. This process helps improve soil fertility and production yield [13]. Rice straws are used for composting or as fodders for livestock. Coconut husks are recycled for use in fiberboards or textile manufacturing [14], while corn cobs and rice hulls are used in household cooking applications. Nevertheless, a large portion of these residues are still underutilized. Some farmers resort to burning to quickly get rid of agricultural residues, which of course may pose environmental and health nuisance [15].

Similarly, livestock production generates substantial amount of wastes mainly in the form of poultry and swine

Table 1 Volume of major crops and livestock residues generated in the Philippines in the year 2016 [12]

Crop/ livestock	Production[a]	Residue	Amount (t)
Rice	17,627,245	Husk	3,767,824
		Straw	8,813,623
Sugarcane	22,370,546	Bagasse	6,163,085
		Cane trash	1,118,527
Coconut	13,825,080	Husk	4,143,376
		Shell	1,970,074
		Frond	13,666,092
Corn	7,218,816	Cob	1,851,626
		Stalk	14,437,632
Poultry	183,429,000	Manure	46,430,446
Swine	22,316,600	Manure	468,648,600

[a] Rice, sugarcane, coconut, and corn: in tons, poultry: birds with 1.5 kg body weight, swine: hogs with 100 kg body weight

manure (Table 1). For swine waste management, large commercial farms venture into waste management and disposal facilities. Most of these include open lagoons for manure storage and treatment, while a few are anaerobic digesters for methane recovery and utilization. On the other hand, backyard farms, which cover 65% of the total hog population, flush wastes out of the pens using water hose. Resulting effluents are then deposited in septic tanks or are directly discharge into nearby streams [16]. In general, only a small portion of these wastes are utilized in anaerobic digesters while bulk of it is being dumped in lagoons or septic tanks, which would eventually cause environmental problems. The disposal of poultry wastes, on the other hand, is not a serious concern in the Philippines as poultry manure is reused or sold to traders as organic fertilizers [17].

2.2 Agro-industrial wastes

Food processing industries in the Philippines like fruit and vegetable processing or distilleries generate very large quantities of organic residues and related effluents. In fact, the Philippines is among the largest contributors of industrial fruit and vegetable processing wastes in the world, generating about 6.53 million t of wastes. These residues are either composted or dumped in landfills or rivers which would ultimately cause environmental hazards [18]. Meanwhile, alcohol distillery companies annually produce an estimated total volume of 2.27 million m^3 of wastewater called spent wash [19]. Spent wash may be used as feedstock for anaerobic digestion to produce methane [20]. However, the disposal of effluents from biodigesters becomes a problem, although efforts are being made to utilize these as fertilizers in sugarcane plantations [9].

2.3 Municipal solid wastes

Municipal solid wastes are derived from residential, commercial, institutional, and industrial sources. In 2016, a total of 40,087.45-t of solid wastes were generated by the municipal sector with an estimated waste generation of 0.40 kg/day per capita [21]. Biodegradable wastes, such as food wastes (expired foods, kitchen scraps), garden or yard residues (leaves and twigs), and paper, constitute 52.31% of these solid wastes. Some municipalities practice composting systems to utilize biodegradable wastes. However, due to the labor-intensive nature and high cost of composting technologies, these systems are not widely adopted. Most municipalities dispose the collected wastes by simply throwing them in open dumpsites which are oftentimes poorly managed hence leading to environmental pollution [22].

3 Biohydrogen production by biological fermentation

Biohydrogen production using organic waste can be achieved by biological fermentation. This process involves the use of microorganisms to anaerobically feed on organic wastes thus forming hydrogen under either dark or illuminated conditions [23]. Accordingly, fermentative hydrogen production process is classified as dark fermentation or photofermentation.

3.1 Dark fermentation

Dark fermentation (DF) is considered as one of the most promising and practical approach for hydrogen production because of its fast conversion efficiency. This method can produce hydrogen from renewable resources like carbohydrate-rich wastes consistently, without a supply of external energy [24]. It involves different groups of bacteria including strict anaerobes such as *Clostridium* and *Desulfovibrio*, and facultative anaerobes such as *Bacillus*, *Enterobacter*, and *Escherichia coli* [25]. Principally, hydrogen in DF is produced as a way for microorganisms to reutilize electrons resulting from the oxidation of organic compounds during their metabolism. It can be produced via different pathways, depending on the species of microorganisms involved, substrates used, and operating conditions [26].

Using glucose as model substrate (Fig. 1), DF starts with glycolysis wherein glucose is converted into pyruvate. The pyruvate is further oxidized to acetyl-CoA and CO_2 through pyruvate ferredoxin oxidoreductase to form reduced ferredoxin. Hydrogen is generated from the reduced ferredoxin via hydrogenase enzyme activity [24, 26]. Via the activity of pyruvate formate lyase, pyruvate may also undergo oxidation forming acetyl-CoA and formate. The latter can be further converted into hydrogen and CO_2 in the presence of hydrogenase. Simultaneously, the acetyl-CoA generated is converted into volatile fatty acids or alcohols such as acetate and butyrate, depending on the type of microorganism and the environmental conditions [27].

Theoretically, complete oxidation of 1 mol glucose will yield 12 mol hydrogen; however, only a maximum of 33% of this value can be produced in the DF processes due to the production of various final products. For instance, the production of acetic acid decreases the hydrogen production from 12 to 4 mol, while formation of butyric acid will only yield 2 mol of hydrogen per mole of glucose [24]. In actual DF operations, a portion of the substrate is utilized for bacterial growth and the metabolism of the substrates may undergo other biochemical routes that do not involve hydrogen production; hence, lower hydrogen yields is usually observed compared to the theoretical yield. Moreover, there is a buildup of acid by-products that causes significant drop in pH and subsequent inhibition of the microbial metabolism, leading to low H_2

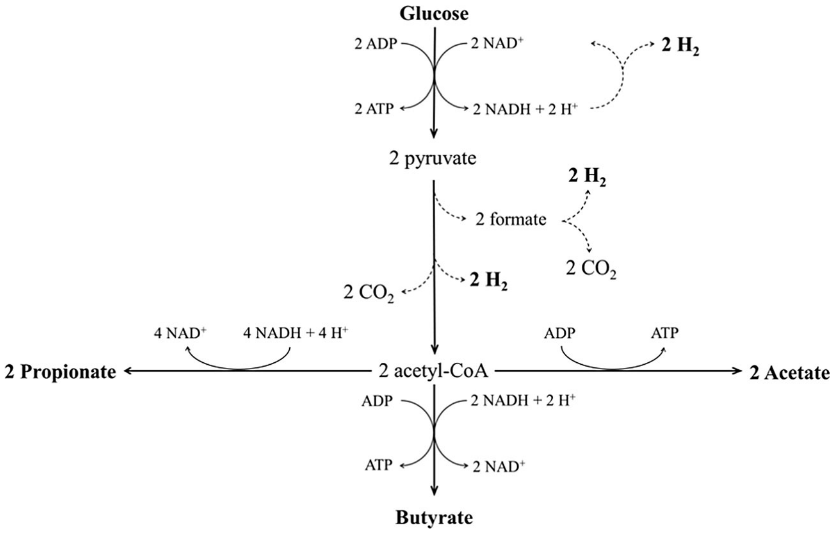

Fig. 1 Metabolic pathway involved in the production of biohydrogen and volatile fatty acid (VFA) from glucose [26]

yields [28, 29]. This is the major drawback of the DF method. On the other hand, volatile fatty acid by-products of DF can be used as substrates in other biological methods to produce more hydrogen. Therefore, the adoption of integrated processes is a promising approach for a complete conversion of biomass resulting in an enhanced hydrogen production [30].

3.2 Photofermentation

Photofermentation (PF) is a process wherein photoheterotrophic bacteria convert organic substrates into hydrogen and carbon dioxide using light energy under anoxygenic conditions [31]. In this method, purple non-sulfur bacteria (PNSB) are the preferred microorganisms because of their capability to generate hydrogen from diverse organic substrates with high yields [32]. Among the organic substrates utilized are fermentation acids such as lactate, acetate, butyrate, propionate [33, 34], and succinate; aromatic acids such as cinnamate and benzoate [35]; alcohols like ethanol and propanol [35]; and sugars such as glucose [36, 37]. The most frequently utilized PNSB for photofermentative H_2 production are species under the genus *Rhodobacter* and *Rhodopseudomonas* [38].

PNSB primarily produce hydrogen under illuminated anaerobic conditions via the activity of the nitrogenase enzyme, and to a lesser extent, using the enzyme hydrogenase. During photofermentation, PNSB transform organic substrates into protons, electrons, and CO_2 using light energy harvested through the aid of light-harvesting pigments such as chlorophylls and carotenoids [38]. This process yields CO_2, protons, and electrons from the tricarboxylic acid cycle. The electrons are then shuttled into cytochrome *c* and undergo a series of electron transfer until they reach ferredoxin. During this photosynthetic electron transport, protons are pumped through the bacterial membrane generating a proton motive force which drives proton translocation of the F_0F_1-ATP synthase and subsequent generation ATP. Under nitrogen-limited conditions, the ATP generated is used to convert protons to H_2 via the nitrogenase enzyme [39]. Meanwhile, hydrogenases in PNSB are involved in regulating H_2 cycling by catalyzing oxidation of H_2 to protons and electrons in a reversible reaction. These enzymes are usually involved in H_2 uptake but can be directed towards H_2 production by manipulating the culture conditions [40, 41] (Fig. 2).

Although a lot of studies show promising conversion yield in PF, most of these are operated under controlled environments using pure bacterial strains which is impractical in a pilot scale setting in terms of energy cost and organic matter degradation for treating organic wastes [42]. Moreover, low

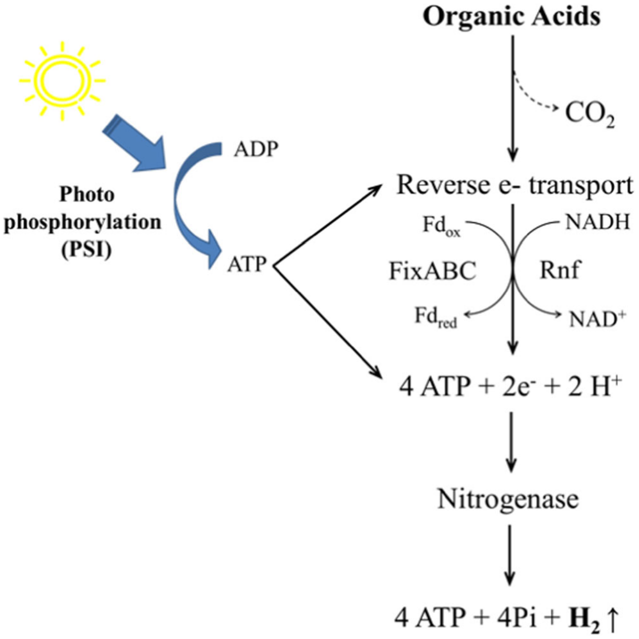

Fig. 2 Biohydrogen production metabolic pathway using photofermentation [41]

light conversion efficiency and low volumetric rates of hydrogen production are frequently observed [43]. Various strategies such as development of low-cost bioreactors and strain improvement by genetic engineering may be implemented to improve photofermentative hydrogen production [44].

3.3 Integrated dark and photofermentation of biohydrogen production

Due to thermodynamic limitations, a single fermentative hydrogen production system cannot achieve the complete oxidation of organic substrates even with fully optimized conditions. A strategy to surpass this challenge is by combining DF and PF to form a hybrid fermentation system. In this approach, hydrogen is produced using DF together with organic acid by-products. These by-products are then utilized as feedstock by PNSB for further conversion into H_2 via PF [31]. The overall reactions of these two processes can be represented as follows:

- Step 1: Dark fermentation

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

- Step 2: Photofermentation

$$CH_3COOH + 2\ H_2O \rightarrow 4\ H_2 + 2\ CO_2$$

As shown, the integration of DF and PF can continuously produce hydrogen at maximum yield using glucose as substrate; hence, this concept is very promising since the hydrogen yield is higher compared to a single DF or PF system.

This hybrid system can be operated as either a (1) combined or single-stage process or as (2) sequential or two-stage process. Combined single-stage approaches employ mixed cultures in which bacteria for DF and PF are directly in contact with each other and perform simultaneously under the same conditions. This operation is very simple and straightforward; however, hydrogen production efficiency is usually compromised because the selection of bacteria is based on compatibility rather than optimal individual performance [45]. On the other hand, the sequential or two-stage approach is more efficient and offer selective advantages over the combined process. It utilizes two different reactors that permits the support of different optimal conditions, and therefore allows for a combination of bacteria which may not be compatible in coculture. However, the cost of this process is relatively high due to the operation and maintenance of two separate reactors. In addition, the effluents from DF often require additional pretreatments before subjection to PF [36]. Nevertheless, owing to relatively low yields from the combined single-stage process, the two-stage approach is more popularly adopted.

Several studies evaluating the performance of two-stage method for hydrogen production using organic wastes as substrate reported significant improvements in biohydrogen yields. In addition, a higher reduction of total volatile solids (TVS) and chemical oxygen demand (COD) was obtained from these fermentation strategies. In the study of Zong et al. [46], the feasibility of using cassava and food waste as substrates for biohydrogen production was demonstrated. The DF step yielded an average of 199 mL H_2 and 22 mL H_2 per gram of cassava and food waste, respectively, and in subsequent PF, the average yield from the DF effluents was 810 mL H_2 and 671 mL H_2. In comparison to single stage DF, the overall hydrogen yield using the two-stage sequential process was increased by 4.08 for cassava and 3.05-fold for food waste. Another study conducted by Yang et al. [47] used pretreated corncob as substrate. The DF and PF yielded a maximum of 120.30 mL and 713.6 mL, respectively, generating a total of 833.9 mL H_2/g corncob. In 2014, Rai et al. [48] used sugarcane bagasse as substrate for two-stage fermentation system. Cumulative hydrogen production yield during DF was 1000 mL/L and 755 mL/L for PF which indicates good potential of utilizing a two-step process for the conversion of sugarcane bagasse into hydrogen. A list of studies that used hybrid systems in treating a variety of organic substrates as well as pure carbon sources is presented in Table 2.

As reported, the use of integrative fermentation systems for hydrogen production is feasible; although at the current status, empirical yields have not yet attained the theoretical values. Possible constraints that limit the hydrogen production include the use of inappropriate operational procedures such pH, temperature, substrate concentration, and light intensity, and the use of ineffective bacterial strains [31]. Nonetheless, investigations are being conducted to find solutions to overcome these technical barriers including immobilization and genetic improvement of bacterial strains, optimization of cultural conditions using statistical approaches, pretreatment strategies of DF effluents for PF, and bioreactor development [76].

3.4 Microbial electrolysis cell for biohydrogen production

Dark fermentation may also be coupled with microbial electrolysis cell (MEC) to further produce H_2. MEC has emerged as a modification of the microbial fuel cell and utilizes a group of microorganisms called exoelectrogens that are capable of oxidizing organic matters. In order to drive hydrogen production, the cathode is contained to keep it from oxygen and a voltage of 0.4–0.7 V is applied [77]. The complete conversion of VFAs into CO_2 and H_2O makes MEC a suitable complement to dark fermentation for treating complex organic compounds [78]. This technology may serve as a good alternative when opacity of wastewater limits PF efficiency. Integrated DF-MEC was shown to produce biohydrogen with reasonable

Table 2 Hydrogen production in a two-stage DF and PF

Dark fermentation	Photofermentation	Substrate	Mode of operation	H_2 yield	Reference
Caldicelluluiruptor saccharolyticus	*Rhodobacter capsulatus*	Potato stem peel	Batch	5.81 mol/mol hexose	[49]
Caldicelluluiruptor saccharolyticus	*Rhodobacter capsulatus*	Beet molasses	Batch	13.7 mol/mol hexose	[50]
Clostridium pasteurianum	*Rhodopseudomonas palustris*	Sucrose	Batch	14.2 mol/mol sucrose	[51]
Clostridium butyricum	*Rhodopseudomonas faecalis*	Glucose	Batch	5.374 mol/mol glucose	[52]
Clostridium butyricum	*Rhodopseudomonas palustris*	Rice straw	Batch	463 mL/g total volatile solid	[53]
Clostridium butyricum LS2	*Rhodopseudomonas palustris*	Palm oil mill effluent (POME)	Batch	3.064 mL H_2/mL POME	[54]
Clostridium butyricum *Enterbacter aerogenes*	*Rhodopseudomonas palustris*	Potato juice and glucose	Batch	8.3 mmol/g COD	[55]
Enterobacter cloacae	*Rhodobacter sphaeroides*	Glucose	Batch	1.86 mol/mol glucose	[56]
Enterobacter aerogenes	*Rhodopseudomonas* sp. BHU01	Cheese whey	Batch	2.04 mol/mol lactose	[57]
Lactobacillus amylovorus	*Rhodobium marinum*	Algal biomass	Batch	7.2 mol/mol hexose	[58]
Mixed culture	*Rhodobacter sphaeroides*	Corn cob	Batch	6.59 mol/mol glucose	[46]
Mixed culture	*Rhodopseudomonas palustris*	Cassava starch	Batch	6.07 mol/mol hexose	[59]
Mixed culture	*Rhodobacter capsulatus* *Rhodobacter sphaeroides*	Distillery wastewater (DWW)	Batch	17.6 L/L DWW	[60]
Mixed culture	*Rhodobacter sphaeroides*	*Chlorella* hydrolysate	Batch	172.2 mL/g VS	[61]
Mixed culture	Mixed culture	Crude glycerol from waste cooking oil	Batch	28 mmol/g COD	[62]
Clostridium butyricum	*Rhodobacter* sp.	Starch	Fed batch	3.6 mol/mol glucose	[63]
Mixed culture	*Rhodobacter* sp.	Sweet potato starch	Fed batch	7 mol/mol glucose	[64]
Mixed culture	*Rhodobacter capsulatus & Rhodobacter sphaeroides*	Potato Starch	Fed batch	5.3 mol/mol hexose	[65]
Citrobacter freundii and *Enterobacter aerogenes*	*Rhodopseudomonas palustris*	Sugarcane effluent	Continuous	2.76 mol/mol hexose	[66]
Clostridium butyricum	*Rhodopseudomonas palustris*	Hydrolyzed Starch	Continuous	3.09 mol/mol glucose	[67]
Clostridium beijerinkii	*Rhodobacter sphaeroides*	Ground wheat starch	Continuous	0.60 mol/mol hexose	[68]
Clostridium butyricum	*Rhodopseudomonas palustris*	Sucrose	Continuous	11.61 mol/mol sucrose	[69]
Mixed culture	*Rhodobacter sphaeroides*	Wheat starch	Continuous	3.40 mol/mol hexose	[70]
Anaerobic sludge	*Rhodobacter* sp.	Wheat powder	Continuous	65.2 mL/g starch	[71]
Bacillus cereus	*Rhodobacter sphaeroides*	Rice husk hydrolysate	Continuous	1.73 mol/mol glucose	[72]
Bacillus cereus	*Rhodobacter sphaeroides*	Rice straw hydrolysate	Continuous	1.82 mol/mol glucose	[72]
Clostridium acetobutylicum	*Rhodobacter capsulatus*	Molasses	Continuous	5.65 mol/mol hexose	[73]
Enterobacter aerogenes	Photosynthetic bacterium HAU-M1	Corn stover	Continuous	90.13 mL/g raw material	[74]
Mixed culture	Mixed culture	Gelatin-rich wastewater	Continuous	0.4 L/g COD	[75]

yields from different organic wastes including corn stalk [79], cassava starch [80], palm oil effluent [81], and various wastewaters [82–84], at a laboratory scale.

Presently, research trends on MEC are directed at enhancing H_2 production rate, lowering energy input, and improving reactor design for an upscale configuration [85]. These bottlenecks, together with the aspect on material cost [86], make MEC difficult to implement on a practical scale.

4 Utilization of organic wastes by fermentative biohydrogen production

Theoretically, any organic substrates that are rich in carbohydrates, proteins, and fats can be feedstock for fermentative biohydrogen production; however, as reported by numerous studies, hydrogen produced during fermentative processes is derived mainly from carbohydrates. Therefore, biomass rich in sugars or complex carbohydrates are the most suitable feedstocks for fermentative biohydrogen production [87].

The most preferred substrates for metabolic conversion by microorganisms in fermentative hydrogen production process are monosaccharides and disaccharides like glucose, lactose, and sucrose, all of which can be found in organic wastes mostly in the form of polymers [24]. These polymers usually possess high level of resistance to chemical and biological degradation because of their complex structure. Hence, pretreatment is necessary to promote hydrolysis and further degradation of these biomass [88]. Pretreatments oftentimes involve drastic conditions in order to transform biomass into a suitable feedstock. The best substrates are those that require less complicated methods of pretreatment and contain significant amount of readily utilizable carbohydrates [24].

Agricultural organic wastes that are plant-based are comprised mainly of lignocellulose materials. These are carbohydrate polymers of cellulose and hemicelluloses that are compactly joined by lignin in a complex manner. Cellulose is composed of glucose while hemicellulose contains glucose, mannose, galactose, xylose, and arabinose as major sugars. These sugar subunits are easily fermentable and are very suitable for hydrogen and organic acid production via DF process [89]. Although common bacterial species used in DF can produce enzymes that hydrolyze cellulose and hemicelluloses into their respective monosugars, the lignin component creates a restriction for these enzymes to access the cellulosic fibers for fermentation; therefore, pretreatment is required for lignocellulosic biomass [30]. Various pretreatment methods that could improve the biodegradation of biomass include physical, chemical, and biological methods. Examples of these are steam explosion, acid/base treatment, ultrasonication, and enzyme treatment [89].

The most common pretreatment method of plant-based agricultural waste for fermentative biohydrogen production is to subject them in acids such as HCl and H_2SO_4. In the study of Fan et al. [90], the use of wheat straw pretreated with acid for DF showed 136-fold increase in hydrogen yield as compared to the use of raw wheat straw. Another study conducted by Zhang et al. [91] found that using acid-pretreated cornstalk for fermentation increases hydrogen yield by 46-fold compared to the use of raw cornstalk. Similarly, Han et al. [92] reported that pretreating soybean straw with acid increased the hydrogen yield by 9-fold compared to the untreated. To further improve the utilization of plant-based biomass for biohydrogen production, acid treatment is coupled with other methods. Nasirian et al. [93] demonstrated that combination of heat and acid pretreatment of wheat straw can significantly improve hydrogen yield. Similar observations were also recorded when applied to corn stover [94] and corncob [95] wastes. Steam explosion as pretreatment, can also improve hydrogen yield as reported in the study of Datar et al. [94] for corn stover and Shanmugan et al. [96] for cornstalk. Likewise, enzymatic pretreatment using cellulases and glucanases can significantly improve hydrogen yield [93, 97]. This can be achieved either by a direct treatment of the biomass with enzymes, or by enrichment with microorganisms that produce these hydrolytic enzymes. Nanoparticles may also be added to cellulose-based substrates to improve H_2 production [98, 99].

Livestock wastes, which include slurry manure, urinary wastes, and farm runoff, are also valuable sources of nutrients that can be feedstock for fermentative biohydrogen production. In the study of Cai et al. [100], it was demonstrated that sewage sludge and dairy wastewater could be used as primary carbon source for biohydrogen production. Kotsopoulos et al. [101] also reported that raw swine slurry can be used for fermentative biohydrogen production under thermophilic conditions. However, generally, only a small amount of biohydrogen can be recovered from the fermentation of livestock wastes due to the low carbohydrate content present in these wastes. Moreover, toxic compounds such as polyphenolic compounds and ammonia which can inhibit growth of microorganisms are frequently found in livestock wastes at relatively high concentrations [102]. On the other hand, several studies reported that livestock wastes provide hydrogen-producing bacteria that are efficient for fermentative biohydrogen production [103, 104]. In addition, co-digestion of livestock wastes and carbohydrate-rich substances showed improvement of biohydrogen yield with a value ranging from 24 to 126 mL H_2/g VS, depending on the type of substrates and bioreactor parameters [102, 105, 106]. Therefore, co-digestion strategy presents a significant advantage for the development of biorefineries where livestock wastes are utilized with other suitable substrates, such as plant-based biomass, for fermentative biohydrogen production.

Wastes from the agro-industrial sector are also good substrates for fermentative biohydrogen production. In particular, residues from the fruit and vegetable industries are considered superior feedstock because they are very rich in carbohydrates and have good moisture content [107]. Other solid wastes and effluents from the dairy and oil industries, sugar refineries, and alcohol distilleries are also suitable and showed promising biohydrogen yield at laboratory scale [108]. In 2010, Mars et al. [109] used untreated potato steam peels for DF and obtained a hydrogen yield ranging from 2.4 to 3.8 mol H_2/mol glucose. Similar yields were obtained by Wang et al. [110] for pineapple wastes. Using sago and tofu-processing wastes, Puad et al. [111] and Kim and Lee [112] obtained hydrogen yields of 2.2 and 2.3 mol H_2/mol glucose, respectively. In both studies, pretreatment such as heat and acid treatments of the substrate were necessary to increase the utilizable carbohydrate content in the feedstock. Protein-rich cheese whey as substrate resulted in a reasonable hydrogen yield of 122 mL H_2/L d from the study conducted by Castello et al. [113]. On the other hand, the use of alcohol distillery wastewater yielded hydrogen production rate of 3310 mL H_2/L d as reported by Searmsirimongkol et al. [114], while a combined molasses and ethanol refinery wastewater generated 1.6 mol H_2/mol hexose [115].

Among the municipal solid wastes, discarded foods and scraps from household or commercial kitchen are the most preferred feedstock for fermentative biohydrogen production. Such wastes are usually high in carbohydrates as well as in proteins and fats [86]. When used as feedstock, solid food wastes are homogenized and added with water to stimulate microbial degradation [108]. In 2000, Okamoto et al. [116] investigated the potential of individual organic fractions of typical municipal solid waste for biological hydrogen production. They obtained a production yield of 31.8–74.7 mL H_2/mg VS, 8.8–61.4 mL H_2/mg VS, 16.8–83.3 mL H_2/mg VS, 1.43–4.8 mL H_2/mg VS, 1.56–3.95 mL H_2/mg VS, 1.31–3.57 mL H_2/mg VS, and 1.75-5.43 mL H_2/mg VS for cabbage, carrot, rice, chicken skin, fat, egg, and lean meat, respectively. In another study, the use of ultrasonicated food wastes from a processing facility yielded 97 mL H_2/g VS from DF [117]. A relatively high amount of volatile fatty acids was observed suggesting the potential of the residual product to be used in PF. Using combined food and paper wastes for DF, Muños-Paez et al. [118] obtained a yield of at least 16.6 mmol H_2/reactor. At the end of their incubation, high concentrations of organic acids were also recorded.

5 Sustainability plan and biohydrogen production potential from organic wastes

With the aim to reduce greenhouse gas emissions from the use of fossil fuels and to increase power generation capacity from renewable resources, the Philippines implemented Republic Act No. 9513 in 2008 which provides a framework for the promotion of renewable energy resources including its development, utilization, and commercialization. The implementation covers various projects including geothermal, hydropower, wind, biomass conversion, and solar power. However, in the aspect of biomass conversion, projects related to biohydrogen production are not yet recognized [119]. To date, not a single policy specific to hydrogen production has been drafted in the country. While hydrogen technology is still in its stage of infancy in highly industrialized nations, the concept of hydrogen economy is yet to be introduced in some developing countries such as the Philippines. At present times, a large portion of the country's economy is being run on existing conventional fossil fuels.

It has been suggested that the European Union will attain a hydrogen-based economy in 2050; while the USA proposed total conversion to hydrogen-powered fuel cell vehicles in 2020 [120]. Embracing a cutting-edge technology such as these would be an enormous challenge for the Philippines as it may entail the formulation of regulatory and safety policies, identification and setup of storage facilities, a revamp of the transportation sector, and solicitation of public acceptance, among other technological and socio-economic endeavors. Nevertheless, if hydrogen economy is going to be an inevitable future, then the country must start identifying its own potential to support such technological revolution. As established previously, hydrogen production using DF-PF may provide a less costly and sustainable waste valorization approach. This review includes a proposed framework for sustainable biohydrogen production in the Philippines and could be a guiding structure for planning and future studies.

Figure 3 shows a sustainable two-stage DF-PF biohydrogen production from organic wastes. The collected organic wastes will be delivered to a processing plant where segregation based on waste type or nutritional value will take place. The organic wastes will then undergo pretreatment and bioprocessing wherein removal of undesirable components as well as nutritional balancing will be achieved. The wastes will then be subjected to acidogenic fermentation or DF. The DF products are H_2-rich biogas and volatile fatty acid (VFA)-rich effluent. The DF gases will be separated using membrane gas strippers [121]. On the other hand, the VFA-rich effluent will be decanted, filtered, or centrifuged to separate the solid and liquid portion of the effluent. The liquid effluent is rich in VFAs and can be utilized for the photobiological H_2 production. The H_2-rich gas will then be purified using a gas stripper, separating the H_2 and CO_2 products of PF. After purification, the H_2 produced will be stored using a specified hydrogen storage tank. The stored H_2 can be used on site or will be distributed or sold to a fuel station or any industries utilizing H_2 as vital component in their operation.

The carbon dioxide emitted during the operation can be injected to a nearby microalgae cultivation pond or bioreactor. Likewise, the wastes generated through the process is a clean type of waste, rich in nitrogen and phosphorous, that may be utilized as fertilizer if it is processed or stabilized properly. Hence, the system is operated in such manner that every end-product is not wasted but rather used up for other special purposes, thus

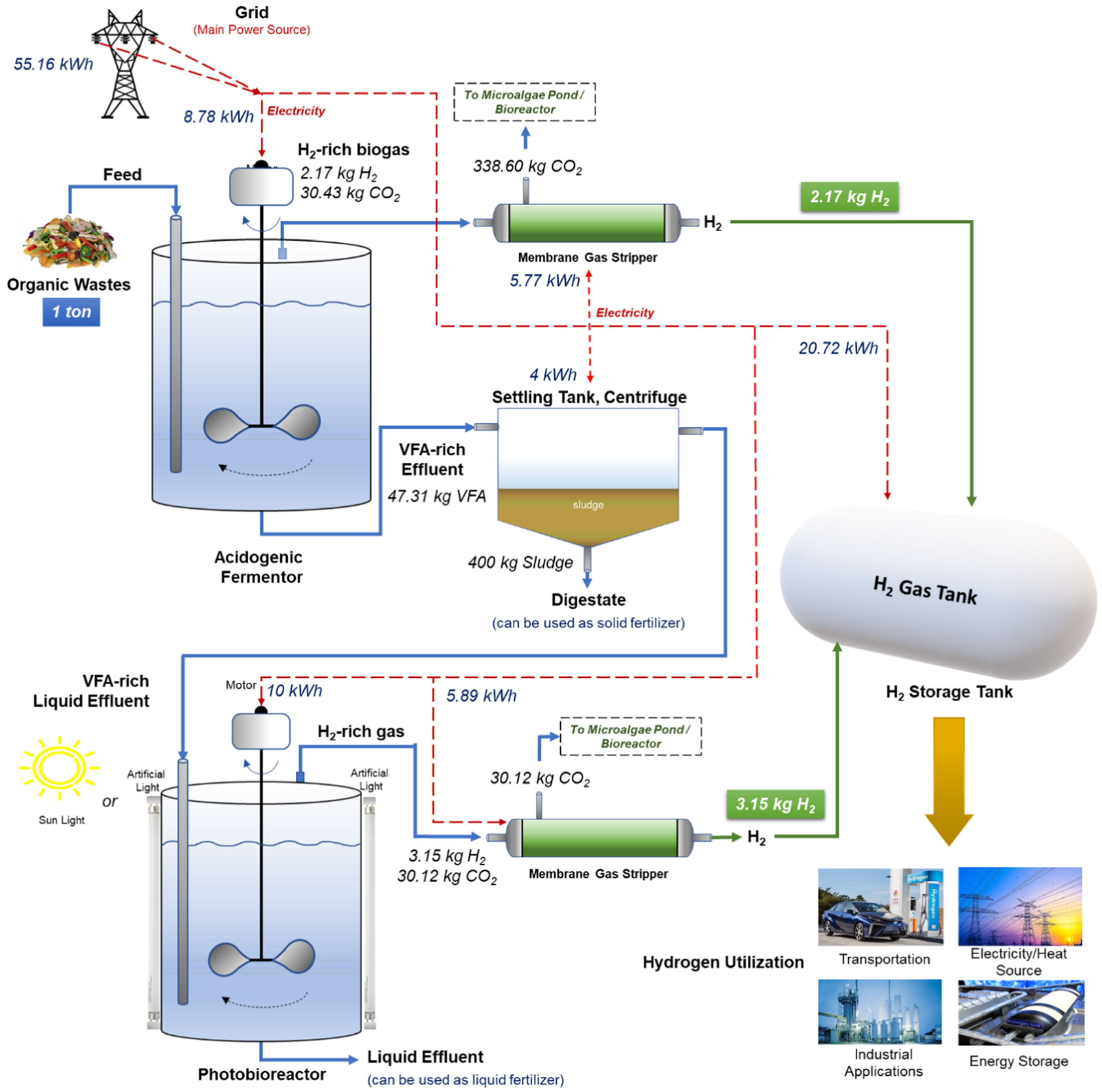

Fig. 3 Schematic diagram of proposed sustainable two-stage DF-PF H_2 production from organic wastes

making the process sustainable and environmentally friendly.

Using a representative biohydrogen production of 1-t food wastes, approximately 5.33 kg H_2 can be produced from the proposed integrated DF-PF scheme (see Supplementary Material for the calculation bases). Approximately 60% (w/w) of the projected total hydrogen production is from the PF stage. Situated in a tropical country, the plant is assumed to be operated at ambient temperature.

In terms of energy requirement per fermentor, operation of PF requires higher energy compared to DF and may be accounted to the added indoor illumination in photobioreactors during cultivation (Table 3). The separation of the DF liquor hydrolysate and sludge requires approximately 4.0-kWh/t organic wastes, while the membrane separation process needs about 6 kWh/t. The compression and storage of the hydrogen produced has the highest expenses incurred which is 37.56% of the total expenditure in the overall H_2 production process. Nevertheless, a biohydrogen energy equal to 177.60-kWh/t organic waste is being projected from the proposed scheme. If to be used as transportation fuel, an output of 106.56-kWh/t organic waste could be obtained considering a fuel cell efficiency of 60%. This amount is still larger than the total energy (55.16-kWh/t organic waste) used to operate the entire system. Hence, this preliminary assessment using data from existing studies could validate the potential and sustainability of an integrated DF-PF biohydrogen.

Using an approximate reducing sugar yield of 30% [48, 53, 122], a reported 1.82 mol H_2/mol hexose on rice straw hydrolysate utilization [72], and theoretical (maximum) 12 mol H_2/mol glucose conversion, the Philippines has the potential to supply an annual hydrogen production of 0.34–2.24 × 10^6 t from crop residues using the proposed DF-PF integrated system (Fig. 4). A large portion of these residues may be

Table 3 Energy consumption of the proposed two stage biohydrogen production using 1-t food wastes

Process	Energy requirement (kWh)	% share
Dark fermentation	8.78	15.92
Settling and centrifugation	4.0	7.25
Membrane separation (dark fermentation)	5.77	10.46
Photofermentation	10.0	18.13
Membrane separation (photofermentation)	5.89	10.68
H_2 compression and storage	20.72	37.56
Total	55.16	

contributed by corn crop farming, with some of the minor shares from rice and sugarcane industries. This shows that the Philippines has a huge capacity of producing its biohydrogen from agricultural crop residues alone.

6 Outlook and conclusion

In response to the growing demand for clean and renewable energy, leading countries have started the thrust towards a hydrogen-based economy. While the Philippines does not currently possess an infrastructure suited for this H_2-technology, it already holds a great potential to produce biohydrogen from its massive biomass wastes. This means that the country should seriously consider H_2 as a potential alternative in addressing the increasing energy demand and reducing carbon gas emissions.

Biological fermentation is a promising hydrogen production method because it uses diverse feedstock including organic wastes from the agricultural, industrial, and municipal sectors whose proper disposal is a major challenge in the Philippines. The utilization of these wastes makes the process economically viable in contrast to other energy-generating methods. As presented in this review paper, a considerable number of literatures demonstrate the feasibility of utilizing organic wastes that can be found in the country, for fermentative biohydrogen production. Nevertheless, research efforts, including the development of pretreatment methods, isolation or genetic improvement of hydrogen-producing strains, and development of optimal operating methodologies and bioreactor configurations through modeling and optimization, are currently being made to address the issues regarding fermentative biohydrogen production. Significant improvements may be expected in the near future.

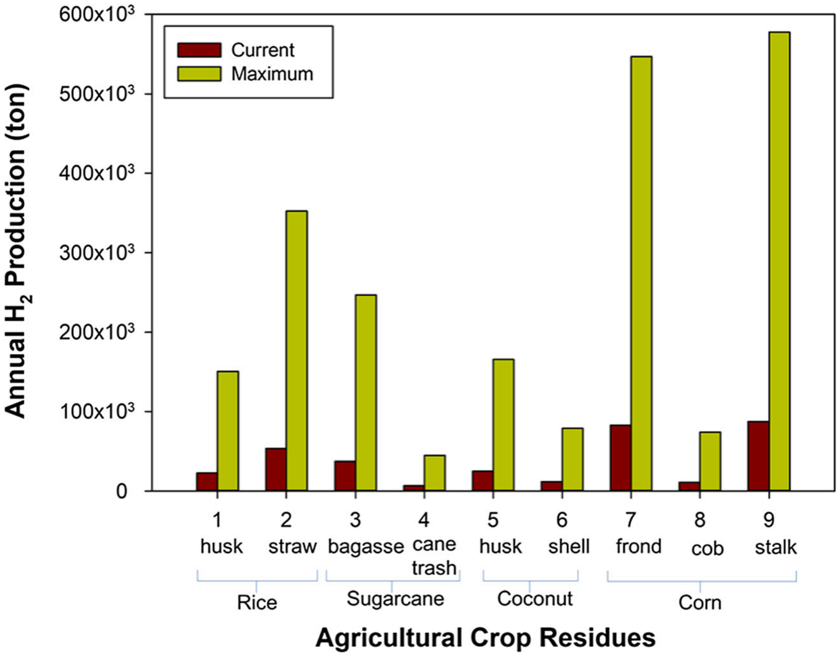

Fig. 4 Biohydrogen production potential of Philippine agricultural crop residues via two-stage DF-PF H_2 production system. The data labeled as "current" were obtained from calculations using existing values from literatures while "maximum" corresponds to the theoretical yield

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Declarations

Conflict of interest The authors declare no conflict of interest.

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