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Microbial electrohydrogenesis cell and dark fermentation integrated system enhances biohydrogen production from lignocellulosic agricultural wastes: Substrate pretreatment towards optimization

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ABSTRACT

The continuous surge in global energy demand, fossil fuel depletion, and related climate change issues have oriented the worldwide researchers' endeavors to the investigation and development of sustainable and cost-effective technology to satisfy the global energy needs. Referring to the non-toxic properties of hydrogen, it is considered as a suitable renewable energy source that could replace fossil fuel-based energy. It is the cleanest energy carrier, combustible with high calorific value, high energy yield. Producing biohydrogen energy from renewable resources such as lignocellulosic agricultural residues could be a sustainable carbon-neutral most cost-effective approach. Dark fermentation has been widely applied as a promising eco-friendly technique to produce biohydrogen from agricultural residues. However, it has shown drawbacks owing to the recalcitrance of lignocellulose structure, and the accumulation of acid-rich intermediate by-products. Microbial electrolysis cells use bio-electrochemical reactions to upgrade H_2 production in a dark fermentation reactor by promoting further decomposition of the generated volatile fatty acids. Therefore, integrating microbial electrohydrogenesis with dark fermentation can be a promising strategy to optimize the straw biomass conversion to biohydrogen. This review aims in delineating the structural composition and recalcitrance of the agricultural residues and their major effects on biohydrogen production. It summarizes all possible pre-treatment methods of the lignocellulosic agricultural residues; elucidates the stable operational conditions of microbial electrolysis cell and dark fermentation integrated system and discusses its performance for biohydrogen production. This study also reviewed the current technical challenges of this integrated system application and suggested sustainable solutions towards its industrial implementation.

1. Introduction

The energy crisis and environmental pollution are two main detrimental issues that are challenging the entire globe. The increasing global energy demand, which could not cope with the available energy supply sources has caused the excessive use of nonrenewable energy reserves [1–3]. The most utilized energy source is a fossil fuel, and its continuous burning leads not only to the depletion of natural resources but also increases greenhouse gas emissions in the air and aggravates the problems of global warming [4]. Therefore, researchers have been used various efforts to investigate and develop a sustainable and cost-effective alternative to satisfy the global energy demands [5–7].

Referring to the non-toxic properties of hydrogen (H_2), it is considered as the most suitable renewable energy source that could replace fossil fuel-based energy [8]. It is a highly combustible gas with a high calorific value (142 kJ/g) and contains a high energy yield (122 kJ/g), which is approximately ~3 times that of fossil fuel-based energy [7,9,10]. Moreover, H_2 the cleanest energy carrier, once burned, produces only H_2O as a by-product which could conspicuously reduce GHG emissions. Thus, adopting hydrogen energy sources as a promising alternative to fossil fuel will not only alleviate the energy crisis but also can prevent environmental disasters caused by climate change. Up to date, several techniques for H_2 production such a steam reforming of

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List of abbreviations

C/N	Carbon/Nitrogen ratio
$CaOH_2$	Calcium hydroxide
CEM	Cation exchange membrane
CH_4	Methane
CO_2	Carbon dioxides
cyt *aa*3	Cytochrome *aa*3
cyt *aa*3	Cytochrome aa_3 oxidase
cyt *bc*1	Cytochrome *bc*1
cyt *bc*1	Cytochrome bc_1 complex
DF	Dark fermentation
$E0_{an}$	Standard electrode potential
$E0_{cat}$	Standard electrode for H_2 evolution
E_{an}	Theoretical anode electrode potential
E_{cat}	Theoretical cathode potential
E_{eq}	Equilibrium voltage
F	Faraday's constant
FADH	Flavin adenine dinucleotide
Fd	Ferredoxin
GHG	Greenhouse gases
H_2 ase	Hydrogenase
H_2	Hydrogen
H_3BO_3	Boric acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
HPP	Partial Pressure of Hydrogen
K	Temperature in Kevin
KOH	Potassium hydroxide
MEC	Microbial Electrolysis cells
MEC-DF	Microbial electrolysis cell and dark fermentation integrated system
NADH	Nicotinamide adenine dinucleotide
NaOH	Sodium hydroxide
PEM	Proton exchange membrane
Q	Quinone
QH_2	Quinol
T	Temperature
V	Voltage
VFAs	Volatile fatty acids
VS	Volatile solid

methane, coal gasification, partial oxidation were applied but reported un-appropriate due to low hydrogen production accompanied by a high amount of greenhouse gas emissions that contribute a lot to destroy our living environment [11]. Therefore, a feasible, cost-effective, and sustainable production of H_2 through environmentally friendly pathways is an emerging technology to overcome the aforementioned challenges.

Agricultural wastes are a great opportunity to recover clean energy, chemical products, and have a big potential for biorefineries application [12,13]. Therefore, converting those lignocellulosic agricultural residues into renewable biohydrogen energy could be a sustainable carbon-neutral and most cost-effective approach [14–18]. This provides environmental benefits like renewable energy generation and straw biomass stabilization which should also be addressed in a circular economy (Fig. 1) [18–24]. Some researchers have used agriculture residues such as wheat, rice, and corn straw as feed-stocks in dark fermentation (DF) for biohydrogen production, but the existence of complex organic polymers in the substrate and generation of inhibitory acid-rich by-products from the acidogenic process led to low hydrogen yield [13]. Dark fermentation is described as the fermentative conversion of organic substrate to biohydrogen in the absence of light. This process includes three main biochemical functions, namely hydrolysis, acidogenesis, and acetogenesis. H_2 products can obtain during the acidogenesis and acetogenesis stages [25].

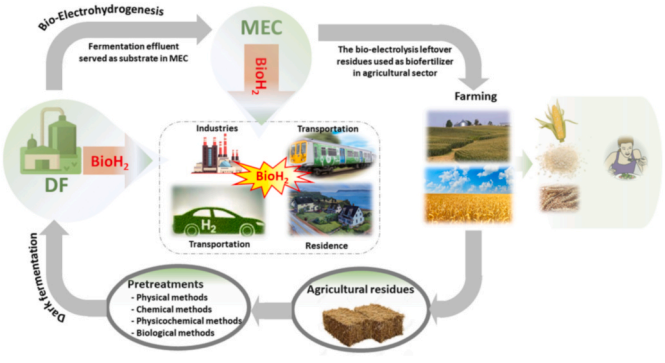

Fig. 1. General schemes of renewable biohydrogen production using lignocellulosic agricultural residues, and simultaneous production of cheap biofertilizers in a combined dark fermentation (DF) and Microbial Electrolysis Cells strategy.

Theoretically, dark fermentation has the potential of degrading the organic compounds in the lignocellulosic agricultural feedstocks to produce H_2 gas [26]. However, the major challenge is the complexity of lignocellulose which makes the wastes recalcitrant to the dark fermentation process [13,27,28], and the thermodynamic limitation that doesn't allow the further spontaneous degradation of the dead-end fermentation products (e.g. Volatile fatty acids (VFAs) to produce H_2. It was also reported that the substrate pre-treatment can effectively alleviate the recalcitrance of the straw biomass by eliminating hemicellulose and lignin, thereby promote the straw biomass biodegradation processes [29]. Therefore, overcoming the above-mentioned barriers, the agricultural straw biomass needs appropriate pre-treatment to improve the efficiency of H_2 production and integrate microbial electrolysis cell (MEC) to dark fermentation to provide the additional energy input required for the continuous decomposition of dead-end products.

Through bio-electrochemical processes, microbial electrolysis cells upgrade H_2 generation in the DF reactors by speeding up the decomposition of complex organic wastes including lignocellulosic agricultural residues and promote further decomposition of the VFAs [30,31]. This approach, supply a low voltage to the dark fermentation system to empower the electrochemically active bacteria for further conversion of the organic compounds to CO_2, protons, and the substantial number of electrons. The anode electrode accepts the generated electrons, then passes through a connecting wire to reach the cathode where are consumed and produce H_2 [31–34]. Therefore, the integration of electrohydrogenesis (MECs) in fermentation processes enhances agricultural straw biomass degradation, thereby leading to high H_2 yield production [34,35].

For further control of the solid organic wastes, researchers proposed that the post-harvest straw biomass could be incorporated into the soils and used as bio-fertilizer, however, the limiting factor to this application, was its recalcitrance property owing to the complex structure of lignocellulose, cellulose, lignin, and its high C: N ratio which impedes its microbial decomposition [13,36]. Meanwhile, other reports proved that the straw leftover residues resulted from the MEC-DF system after undergoing bio-degradation and electrochemical decomposition during the biohydrogen production, enrich essential nutrients such P, N, K, Mg, Ca, …etc, which are indispensable for plants growth [36,37]. Therefore, the application of the generated leftover residues in the agricultural sector and serve as a natural biofertilizer to promote soil quality, instead

of leaving them in the open environment where they could cause other detrimental problems such as polluting the environment and affect human health, would be highly encouraged. This application would be more economical, non-polluting, and renewable based-energy sources.

Recently, there are plenty of reviews that provide general information on the hydrogen production from wastes through biological technics that include direct and indirect biophotolysis, and photo-fermentation [38,39]. Some other researchers also reviewed the dark fermentative biohydrogen production from lignocellulosic biomass [40–42] and reported different technics such as combining dark fermentation and photo-fermentation [43], dark fermentation, and heterogenous catalysis [44] to improve the hydrogen production yield. However, to date, there is no recent work reviewing the feasibility of employing the combined dark fermentation and bio-electrohydrogenesis processes, and stable operational conditions as a sustainable way to enhance the biohydrogen yield from lignocellulosic agricultural residues. This review aims to explore the performance of MEC technology coupled with dark fermentation for promoting biohydrogen production from agricultural straw biomass as feedstock, it discusses all possible pre-treatment methods of lignocellulosic agricultural residues for biohydrogen yield promotion and elucidating the optimum operational conditions of MED-DF techniques for sustainable applications. This review also revealed the current technical challenges of this strategy and suggests sustainable solutions towards its industrial implementation.

2. Global production of straw and its characterization

2.1. Worldwide distribution of straw wastes

The agricultural sector disposes of large quantities of straw wastes all over the world. Annually, ~7 billion tons are being generated, and 900 million tons of it, is produced from china alone [45]. 90% of the total generated straw are rice, wheat, and corn straw [45,46]. The annual global rice straw production is approximately 731 million tons and 1.7, 3.9, 20.9, 37.2, and 667.6 million tons of it, are generated from Oceania, Europe, Africa, America, and Asia, respectively [46,47]. The world wheat straw production is about 584 million tons, and its big portion comes from Europe (140 million tons), followed by America, Asia, Oceania, and Africa with 65, 16, 10, and 7 million tons respectively [46]. Cultivation of maize is also considered as the third main source of straw biomass, which produces about 230 million tons at a global scale. America disposes of 150 million tons, followed by Asia, Europe, Africa, and Oceania with 45, 31, 3.5, and 0.5 million tons respectively [46]. Therefore, straw biomass is the most generated agricultural residues on this globe. It has potential applications in human society, such as a quality cattle forage, fertilizer, and heating fuel source since it has a lot of heat energy potential in it [48]. Wheat Straw, corn stover, switch grass, and others were also reported to serve as potential raw materials for the productions of a variety of products that include biofuel, ethanol, polymers, bioplastic, and production of materials for construction, furniture, and baskets [48–50].

2.2. Straw biomass composition and its recalcitrance for hydrogen production

Lignocellulosic agricultural residues contain C6 and C5 sugars (such as glucose, mannose, xylose, and arabinose), which can be used as a raw material for biohydrogen production. However, the presence of lignin hinders the processes that produce biohydrogen and the conversion efficiency of the agricultural straw biomass [51]. The recalcitrance of lignocellulosic biomass straw refers to their building structures which naturally contribute a lot to prevent their biodegradation, thereby lead to lower simple sugar production which inevitably decreases biohydrogen production efficiency. Straw wastes are generally composed of hemicellulose, cellulose, and lignin like all other lignocellulosic biomass (Table 1) (Fig. 2) [13]. Cellulose is the main constituent of the plant cell wall and its polymerization degree and crystallinity negatively affect the enzymatic hydrolysis reactions during the H_2-fermentative production process [52,53] and it gives the primary backbone to lignin-carbohydrate complexes (Fig. 2). The hydrogen and covalent bonds with the van Der Waals force present in the cellulose molecules maintain its straight nature, and the interchain hydrogen bonds controls the structural arrangement [51].

Hemicellulose is composed of various monosaccharide units and its main component is xylan which is consisted of the backbone chains of 1, 4-linked b-d-xylopyranose (Fig. 2). Its matrix contains crosslinking agents such as monosaccharides, ferulic acid, and many other side chains which made it a very complicated structure that cannot easily be hydrolyzed [54,55]. The covalent bonds between hemicelluloses and the cellulose fibrils surface, help in further strengthening the cell wall complex structure [54]. The lignin compounds cover the blanks of hemicellulose and cellulose chains and create a hydrophobic lignification to maintain the cell wall structural integrity (Fig. 2) [28,56]. A formed recalcitrant three-dimensional structure of lignin makes it inaccessible to bacterial degradation [57]. Lynd et al. reported that the crystalline complex of lignocellulose impedes its decomposition at the early stage, thus become one of the limiting factors of biohydrogen production [58].

In contrast to hemicellulose and cellulose, lignin consists of phenylpropane units and it is believed to be the main biodegradation-limiting factor of agricultural wastes. It hinders the bioconversion of straw biomass to biohydrogen, due to its contribution in restricting the biodegradation of polysaccharide-like structures through enzyme-catalyzed reactions [13,60]. Moreover, the proteins embedded in the cell wall, lipids, pectin, mineral, and other organic compounds notably contribute to the straw waste recalcitrance [28,61]. Furthermore, the epidermal protection, the density and vascular bundles arrangements, and even some process-induced causes contribute a lot to build the plant cell wall matrix (Table 2) [13]. Therefore, the lignocellulosic biomass has an anti-degradation property caused by a sophisticated combination

Table 1
Straw characterization and macromolecular composition (Redrawn from Ref. [62]).

Feedstock (straw)	TS ($g.kg^{-1}$ ww)	VS ($g.kg^{-1}$ TS)	Lignin ($g.kg^{-1}$ TS)	Hemicell. ($g.kg^{-1}$ TS)	Cellulose ($g.kg^{-1}$ TS)	Carbon/Nitrogen (C/N)	References
Maize	940	874	87.2	281	412	71	[63]
Maize	940	900	90	280	400	70	[64]
Rice	973	863				59	[65]
Rice	910	740	190	200	280		[66]
Rice	903	857	65	298	300	70	[67]
Rice	958	840	67.8	281	454		[68]
Rice	954	839	171	501	215		[69]
Wheat	940	865	9	242	450	81	[70]
Wheat	895	821				92	[71]
Wheat	942	889	75	256	351	109	[72]
Wheat	920	860					[73]

TS: Total solids; VS: Volatile solid.

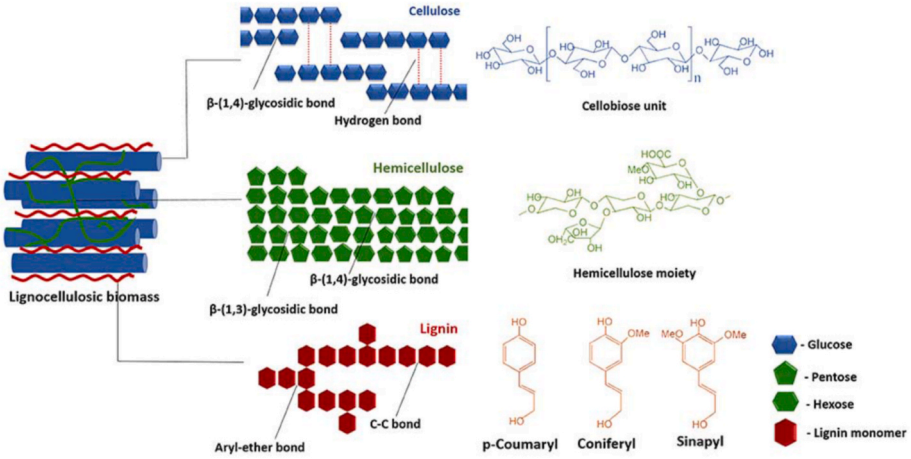

Fig. 2. Structure components of lignocellulosic straw biomass. (Adapted from Ref. [59] with permission of Frontiers. copyright 2018).

Table 2
Factors making lignocellulosic straw biomass recalcitrance (Redrawn from Ref. [28]).

Factors	Relative effects	References
Epidermal protection	The epidermal tissue of the plant body, particularly the bark, cuticle, and epicuticular waxes	[79,80]
Cellulose characteristic	A high degree of CrI and DP of cellulose challenges for enzymes acting on an insoluble substrate	[13,81]
Chemical compositions	Heterogeneity and complexity of constituents, degree of lignification, and complexity of chemical cross-linkages	[82]
Cell wall physical structure	Arrangement and density of the vascular bundles; the relative amount of sclerenchymatous tissue	[55,81]
Process-induced causes	Inhibitors are generated during conversion processes (e.g., cellulose realignment)	[13]

of complex building blocks of the plant cell wall (Fig. 2) [28].

Another limiting factor for biohydrogen production from agricultural residues is its uncommon feature of high C/N values reaching ~80 which inhibits the electrochemically active bacteria growth [72,74,75]. However, based on the straw biomass's nutritional composition, they could be employed as a suitable feedstock for renewable biohydrogen energy generation [7,62,76–78].

3. Pretreatment methods of agricultural straw biomass and seed inoculum preparation for biohydrogen yield promotion

3.1. Pretreatment methods of lignocellulosic agricultural residues

To eliminate and control the straw biomass recalcitrance is an effective way to improve hydrogen production from agricultural residues. In that regard, lots of pretreatments' technics have been investigated to convert complex lignocellulosic structures into readily biodegradable simple sugars. Many researchers recently reported that the straw biomass pretreatment helps the conversation of cellulose and hemicellulose to monosaccharides in the hydrolytic reactions catalyzed by bacterial enzymes [51,83–85]. The biohydrogen-producing microorganisms, through bio-electrochemical reactions, biodegrade these monomers and produce biohydrogen with other fermentative by-products. Prior to biohydrogen production, the recently studied pretreatment methods of the straw biomass for biohydrogen yield promotion are grouped into physical (milling, grinding, ultrasonication, extrusion, and microwave and irradiation pretreatment), physicochemical (ammonia fiber explosion (AFEX), steam explosion, liquid hot water, and SPORL), chemical (alkaline hydrolysis, ozonolysis, organo-solvation, oxidative delignification, acid hydrolysis, and ionic liquids); and biological (fungal, bacterial and enzymatic) pretreatments [13,41,51,85–87]. The detailed discussion of pretreatment methods is summarized in Table 3.

3.1.1. Physical pretreatment of straw biomass

The pretreatment which doesn't involve either chemicals or microbial populations is defined as physical pretreatment. Generally, the starting physical pretreatment process of the straw biomass is comminution (milling, grinding, extrusion) which remarkably reduces the size of the substrate, changes the ultrastructure, minimizes the crystallinity and polymerization degree of cellulose, and increases the accessible surface area for microorganisms for improved digestibility [88] (Table 3). Extrusion pretreatment involves a sequence of treatment strategies namely heating, mixing under high pressure by employing the extruder. This whole process ensures the disruption of the complex structures of the lignocellulose which subsequently promotes the generation of readily digestible sugars for fermentative biohydrogen evolution [59,89]. The ultrasound application for agricultural residues pretreatment was reported to significantly disintegrate the lignocellulosic structures, depending on the selected operating conditions (temperature, oscillation frequency, and the operating time) [90]. For example, in 2018, Kucharska et all. reported high delignification efficiency at the sonication frequency of 40 kHz during lignocellulosic biomass pretreatment [90]. Microwave and Irradiation are used to break down the glucoside bonds and decompose the cellulose chains into breakable fibers and oligosaccharides [91]. This pretreatment method speeds up the degradation of the complex biopolymers and thereby enhanced the fermentation processes for biohydrogen production. The crystallinity of cellulose was also significantly decreased 51%–32% during gamma radiation pretreatment of the biomass [90,92].

Irradiation, normally considered as physicochemical pretreatment, is used to break down the glucoside bonds and decompose the cellulose chains into breakable fibers and oligosaccharides [91]. This pretreatment method speeds up the degradation of the complex biopolymers and thereby enhanced the fermentation processes for biohydrogen production. It has been shown that the application of physical pretreatment alone, generally increases the biohydrogen, methane, and ethanol by 5–25% compared to the non-treated biomass [29,90,92]. However, the noticeable drawback of the physical pretreatment is its incapacity to eliminate the lignin structure, which thus limits the access of the enzymatic reactions to cellulose [90,93,94]. Besides, these methods consume high energy amounts which don't correlate with the low hydrogen yield produced during the dark fermentative process. It is costly for its industrial application perspective and is always accompanied by

Table 3
Most recent methods applied in lignocellulosic agricultural residues pretreatment prior to fermentative biohydrogen production.

Pretreatment methods	Example	Effects	Advantages	Disadvantages	References
Physical methods	Milling, chopping, grinding,	Substrate size is reduced and split crystalline complex, larger surface area, and pore size	Crystalline complex and substrate size are both reduced, and no toxic of inhibitory byproduct generated	High capital cost, high energy consumption	[41,90, 122,123]
	Microwave irradiation	Lignocellulosic agricultural residues as swollen and fragmented	Simple and low energy-consuming process, low inhibitor generation, a quick process with short reaction time, solvents or auxiliary chemicals are not used	The radiation inflow in the substrate is low	[41,90, 122,123]
	Sonication (ultrasounds)	Cleavage of chemical bonds, larger surface area	The disintegration of the lignin structure	High Energy consumption	[90,122]
	Spray drying with gamma radiation	Rapture of −1,4 glycosidic bonds	Reduces the crystallinity, Low inhibitors production	High energy consumption	[90]
	Extrusion	Substrate size is reduced, and breakdown crystalline complex	Destruction of cellulose structure, increase the surface area	High energy consumption	[89,122]
Chemical methods	Alkali	Cleavage of lignin, dissolution of hemicellulose, increase of internal surface area, reduction of polymerization	Significant removal of lignin from the agricultural residues, and accompanied by low inhibitor production	The high cost of the alkaline catalysts, alteration of the lignin composition, long residence time required.	[41,59,90, 122]
	Acid	Lignin cellulose and hemicellulose fractionate, alteration of cellulose structure	The appreciable yield of glucose, hemicellulose is completely solubilized, short reaction time.	The high cost of acid (catalysts), generate toxic and inhibitors, cause corrosion to the used materials	[41,59,90, 122]
	Oxidative and ozonation pretreatment	The disintegration of hemicellulose and lignin structures, cellulose crystals separation	Removal of hemicellulose and lignin	Chemical cost, formation of inhibitors	[89,90]
	Organic solvent pretreatment	Removal of lignin and break down of hemicellulose	Increases the purity of lignin	Costly, solvent separation and washing process requirement	[122]
	Ionic liquids	Cellulose precipitation and lignin removal, reduction of crystallinity	Effective disruption of cell wall structures in the ambient environment, mild operating conditions, the thermal stability is high, low volatility, and the reagents are reusable.	High cost of the solvents, the necessity of recycling the solvent, Inhibits the enzymatic reactions, the complexity of purification and synthesis	[41,122, 124]
Physicochemical methods	Liquid hot water	Removal of lignin and the hemicellulose structure is partially hydrolyzed	Separation of pure hemicellulose, the catalyst is not required, not toxic or inhibitors generated, washing step not required	Consumption of a high amount of water, and requires high energy input.	[41,59, 122]
	Ammonia fiber explosion (AFEX)	The crystallinity is disrupted and reduced, and remove lignin, an increase of cellulose accessibility	Accessibility of cellulose, low generation of toxics and inhibitors	The necessity of reprocessing ammonia, high cost of commercial ammonia, not applied for biomass with lignin content	[41,59, 122]
	Steam explosion pretreatment	Reduction of the substrate size, hemicellulose is partially hydrolyzed, accompanied with lignin removal	Hemicellulose and lignin are hydrolyzed, destruction of cellulose crystallinity, fewer water uses, doesn't need other chemicals, eco-friendly process.	High energy demand and capital cost, recalcitrant compounds formation	[41,89, 122]
	SPORL	Removal of lignin and break down of hemicellulose	Low generated inhibitors, energy-efficient, ability to decrease the absorption by sulfonation of cellulose	High cost of chemical recovery	[122]
Biological methods	Fungal pretreatment: • White rot fungi • Brown rot fungi • Soft rot fungi	Delignification and partial hydrolysis of hemicellulose, alteration of lignocellulose structure	Reduces lignin and hemicellulose, low energy necessity, cost-efficient, environmentally friendly	Long pretreatment time, Low hydrolysis speed, easily contaminated, and long incubation periods	[41,90, 122]
	Bacterial treatment (*Zymomonasmobilis, Escherichia coli*)	Hemicellulose and lignin decomposition	Disrupt and decrease lignin and hemicellulose, require low energy, cost-efficient, environmentally friendly	Long pretreatment time, Low hydrolysis speed, easily contaminated, and long incubation periods	[41,59,90, 122]
	Enzymatic pretreatment Cellulase, α-amylase, xylanase.	Hemicellulose and lignin decomposition	Generate zero toxic and inhibitors, eco-friendly process with no harsh conditions	Slow process with low enzymatic hydrolysis rate	[41,90]

environmental and safety concerns [90,93,95].

3.1.2. Physicochemical pretreatment

The physicochemical methods use oxidation and thermal treatments to decompose the lignocellulosic polymers. For example, the steam explosion method employs high-pressure at elevated temperatures to pretreat the agricultural residues whereas the ammonia fiber explosion strategy uses ammonia (liquid state) at high temperatures. They both hydrolyze the hemicellulose and decrease lignin content to some extends, which thus leads to the entire lignin-carbohydrate complex decomposition. For better performance, they are always assisted by additional acids and other chemicals [96,97]. These pretreatment methods have been successfully used by many researchers to treat various lignocellulosic biomass including straw biomass for bio-hydrogen production [98].

The liquid hot water method uses water at high temperature and pressure, it augments the accessible surface area of agricultural straw biomass and improves cellulose biodegradability to cellulase. Hot water first invades the internal structure of the cell, dissolve hemicellulose, moderately eliminate lignin, and hydrate cellulose (Table 3).

Researchers reported that this method gives rise to very little corrosion to the manipulating system and generates fewer byproducts and inhibitors. It is therefore considered as a potential method for pentose recovery that serves as raw material for biohydrogen production [99,100].

3.1.3. Chemical pretreatment of agricultural straw biomass

Chemical pretreatment was used by many researchers to change the physical and chemical properties of the agricultural straw biomass with the help of other chemicals such as bases, oxidizing agents, acids, and other organic solvents. Acid pretreatment strikingly hydrolyzes hemicellulose to simple monosaccharides, disrupt lignin to a high extent and make cellulose compounds more sensitive to enzymatic decomposition [13,101] (Table 3). The solubilization degree of lignin depends on the concentration level of the used acid [51]. The commonly used acids are H_2SO_4, HCl, HNO_3, and H_3BO_3. Cao et al. used dilute HCl (0.25–4% v/v) to pretreat corn stover for promoting biohydrogen production at 121 °C for 30–180 min. As a result, the employed 1.6% of acid achieved a maximum biohydrogen yield of 3305 mL H_2/L medium within 117 min [102]. Some other investigators have also worked on combining alkali and acid pretreatment of agricultural wastes to improve the biohydrogen production and proved that employing 10% ammonia and 1% dilute H_2SO_4 for the pretreatment of rice straw biomass could increase the digestibility up to 85% [103], and convert 72% of glucose and 95% of xylose into biohydrogen [51]. Another researcher also pretreated palm oil fruit brunch by using 6% of H_2SO_4 for bioH_2 production, and he achieved a maximum biohydrogen yield of 690 mL/L. The simple sugar productions also increased by 78% with acid pretreatment [51,104]. Referring to the cost, toxic by-products, and demanding materials, dilute acid was preferably used in practical application [105,106] (Fig. 3).

However, the most investigated and employed pretreatment method is the alkaline process. It causes the degradation of ester and glycosidic bonds between the hemicellulose and lignin, which results in the significant decrease of the lignin content and partially prompts the dissolution of the hemicelluloses, and subsequently induces the solvation and saponification reactions [107]. Due to the above reactions, the feedstock dilates and the organic compounds become more accessible to microorganisms. The most employed alkalis to pretreat the agricultural straw biomass for biohydrogen yield evolution, include NaOH, KOH, and $CaOH_2$ [51].

Solvation breaks down the lignin complex and splits the linkages between lignin and other structures, which thus remarkably removes lignin and especially the acetyl group and uronic acid of hemicellulose (Table 3). Chandra et al. have proved that the treatment of straw wastes with NaOH was so advantageous due to the noticeable increment of the biogas production 87.5%, which included a high yield of biohydrogen as well [72,75,108]. Khongkliang et al. showed that the biogas generation increased by 40% when employing ammonia as the alkaline pretreatment method on straw biomass [109], and Panagiotopoulos et al. used 10% of NaOH to pretreat sweet sorghum bagasse for promoting the production of biohydrogen yield and achieved 46% delignification and a maximum biohydrogen yield of 10.2 mmol/L in an hour [110]. Cao et al. also used lime as an economically competitive alternative to NaOH, to pretreat corn stalk for biohydrogen production (0.1 g for 1 g of corn stalk), and obtained 38% higher biohydrogen yield than that of the untreated biomass [111] and 23% of lignin was removed.

The use of ionic liquids was also reported so advantageous because of being accompanied by low toxicity, low hydrophobicity, thermal stability, and improved electrochemical stability [112]. At mild conditions, the ionic pretreatment of agricultural straw biomass massively solubilize cellulose and could reclaim ~100% of the used liquid with high purity. Straw biomass enters ionic liquid (IL) pretreatment at 120–140 °C with 1-ethyl-3-methylimidazolium acetate (EmimAC). After certain hours, the products are washed by anti-solvent and lead to cellulose regeneration. The cellulose is then extracted, lignin is precipitated, and give rise to anti-solvent recycle and IL (Fig. 4) [113,114].

During ionic liquid processes, the cellulose is dissolved owing to the disintegration of the H_2 bonds between its molecules, however, it is then reformed by adding the specific precipitate cellulose-forming solvents [115,116]. Compared to the primitive cellulose from the straw waste, the formed cellulose precipitate has a high enzymatic digestibility due to the occurred modifications in the intra-structure; and the difference in crystallinity characteristics [117]. In 2016, N-methylmorpholine-N--oxide (NMMO) ionic liquid was used by a researcher to pretreat cassava residues prior to enzymatical hydrolysis and production of fermentative biohydrogen and reported an improvement of the reducing sugar yield from 36 to 42 g/100 g cassava residues, the crystallinity coefficient decreased from 40% to 34%, and hydrogen yield increased from 92.3 to 136 mL/g TVS [118]. Another researcher reported the biohydrogen yield increment of 38.4% after using pretreated cellulose with 1-butyl-3-methylimidazolium chloride *[C4mim]Cl* as IL in DF with *Thermotoga neapolitana* [92,119]. Even though the ionic liquids pretreatment increases the H_2 yield, the high operating temperature generates unwanted compounds that may hinder biohydrogen production [92].

During organo-solvation pretreatment of straw biomass, an organic solvent is employed to split the bonds of either lignin or hemicellulose, thus resulting in making available simple monosaccharides susceptible to microbial degradation [66,69]. This pretreatment method has been reported by many researchers to increase biohydrogen and other biogas production from lignocellulosic wastes [66,69]. Furthermore, the ozonolysis method also is commonly used to demote the lignin amount within the straw or other lignocellulosic agricultural residues (Table 3). The application of ozone pretreatment does not produce toxic residues, and it has been reported to remarkably increase the digestibility of the treated substrates [120]. This pretreatment process has significantly promoted biogas production by 45% from wheat straw biomass [121]. Though, they are several investigated chemical pretreatment methods, using acid and bases are conventionally often used for lignocellulosic agricultural residues pretreatment and are considered as a low-cost process for biohydrogen production, however, this process inevitably generates along with inhibitors as byproducts. Therefore, the current

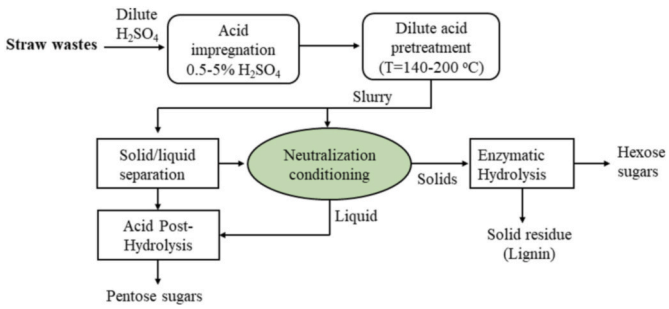

Fig. 3. Illustrating diagram of the sulfuric acid pretreatment process.

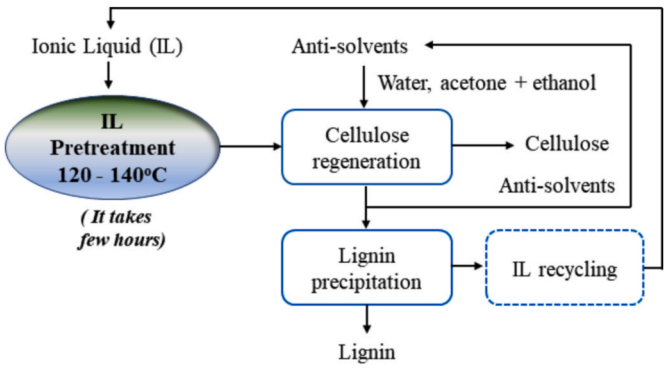

Fig. 4. Illustrating diagram of the ionic liquid pretreatment process.

research direction suggests that those generated by-products during chemical pretreatment be purified and reused as value-added products instead of negatively affect the biohydrogen production by inhibiting microbial and enzymatic biocatalysts. If successfully approved, it may be an economic approach for lignocellulosic biomass bioconversion processes for biohydrogen evolution [90].

3.1.4. Biological pretreatment of lignocellulosic agricultural wastes

Biological pretreatment uses fungi, bacteria, and enzymes to change the structure and chemical properties of the agricultural straw biomass and makes them more accessible to enzymic digestion for biohydrogen production. Fungal pretreatment of agricultural straw biomass was reported as a suitable application for enhancing the production of biohydrogen yield since it is capable of degrading cellulose, hemicelluloses, and lignin. Fungi such as white-rot, brown-rot, and soft-rot were commonly used in biological pretreatment of the agricultural straw biomass [59]. The application of a white-rot fungi *Irpex lacteus* to pretreat corn stalk produced various hydrolytic and oxidative enzymes and achieved the hydrolysis yield of 82% within 28 days [59,125], whereas, *phanerochaete chrysosporium* enhanced biohydrogen production and achieved the delignification of 34% and the enzymatic saccharification increased by 20% higher than the untreated biomass [126]. Fungi pretreatment possesses two important systems, which include the oxidative ligninolytic system responsible for breaking down the phenyl bonds in lignin, and the hydrolytic enzyme process which decomposes hemicellulose and cellulose (Table 3) [127]. This method conspicuously biodegrades lignin, and thus promotes the cellulose digestibility for normal fermentation [128].

The aerobic bacteria were also characterized by their high potentials for agricultural residues decomposition, the ability to promote the bond cleavage between Cα-oxidation and Cβ-Cβ in the lignin polymer, and have the major advantage of having a faster growth rate than fungi [89,129]. The co-culture of *Bacillus* sp. in agricultural residues has been reported to significantly reduce the lignin content and *Citrobacter werkmanii* VKVVG4 improved the solubilization of water hyacinth during fermentation processes [89,130]. The enzymatic pretreatment methods of lignocellulosic agricultural residues were also investigated and improved the biohydrogen yield. It uses commercial pure enzymes or from other bacterial species to speed up the biodegradation of lignocellulose present in the straw biomass.

The most-reported enzymes in this scenario include cellulase, endoxylanase, amylase, bromelain, hemicellulase, and lignin-degrading enzymes (lignin peroxidase, laccases, manganese peroxidase, and versatile peroxidase) [51,131]. Quemeneur et al. employed exogenous enzymes for wheat straw pretreatment to enhance biohydrogen production and reported that the biohydrogen production increased from 10.5 mL to 19.6 mL of biohydrogen per 1 g of volatile solids (VS), as compared to the untreated one [132]. Through the enzymatic actions, the easily biodegradable sugars are produced from cellulose and hemicellulose, thus definitely enhance hydrogen production from straw biomass. However, the enzymatic pretreatment of the lignocellulosic biomass prior to fermentative biohydrogen production was reported to produce low biohydrogen yield which does correlate with the high cost of the applied enzymes [133]. Therefore, the application of this method is not practical owing to the involvement of the high cost of the used enzymes and low biohydrogen production.

It is noteworthy that, each above discussed method has its particular impact either on physical or chemical properties of the straw biomass intractableness, which includes: reducing crystallinity and polymerization, augmenting accessible surface area, and eliminating lignin content, and subsequentially enhance biohydrogen production under anaerobic fermentation (Table 3). Selecting the suitable pretreatment method should refer to several factors, like avoiding the formation of the by-product that could hinder the microbial activities, the kinds of agricultural straw biomass, the downstream bioconversion reactions, and the preliminary treatment cost.

3.2. Seed inoculum preparation for biohydrogen promotion

The possibility of producing biohydrogen using a mixed microbial culture is unsuggested due to the H_2 consumption by methanogens [134,135]. Therefore, it is wise to pretreat the parent bacterial inoculum for altering the cell metabolism to promote acidogenesis and inhibiting the methanogenesis process to happen, thereby enhancing hydrogen generation [92,136,137]. Many researchers have suggested various parent biocatalysts pretreatment technics such as heat shock (above 80 °C), chemical approach (using 2-bromoethanesulfonic acid, Na_2SO_4, acetylene, chloroform, iodopropane, and fluvastatin, for inhibiting specific metabolic functions), alkaline shock (carried out under pH > 9), acid shock (operated under pH < 4), load shock (higher substrate concentration), an oxygen shock approach (oxygen/air), freezing and thawing, and infrared irradiation [134,135,138–140]. Biocatalyst pretreatment is certainly used to parent inoculum and it helped to choose the bacterial consortia responsible for acidogenic reactions and concurrently generate a high amount of hydrogen and inhibit the hydrogenotrophic methanogens [92,141]. Moreover, this method can noticeably provide the central basics for the establishment of an H_2 production system due to the obvious physiological differences between the biohydrogen-consuming microorganisms and biohydrogen-producing acidogenic microorganisms [39,136].

Recently, another active research direction is the exploration of the feasibility of using the metabolically engineered bacterial strains to directly enhance biohydrogen production from agricultural residues. In some hydrogen producing-bacteria species produce inappreciable biohydrogen yield, therefore to apply genes encoding uptake hydrogenases, overexpression of hydrogen-evolving hydrogenases, hemicellulases, cellulases, and lignin-modifying enzymes that favor the availability of simple sugars (glucose), and inhibit or suppress all other metabolic pathways that compete for biohydrogen generation is the best way to enhance the bacterial metabolic reactions leading to the enhanced biohydrogen production [142,143]. These techniques have been previously investigated and employed to promote fermentative biohydrogen production. For instance, in 2019, Li et al. employed the genetically modified *T. aotearoense SCUT27* to promote hydrogen production and reported the remarkable increase of ~42% after deleting *nfnAB,* and thereby suggest that *T. aotearoense* SCUT27/*ΔnfnAB* could be **a** promising target strain for biohydrogen production from agricultural residues [143]. After deleting *nfnAB* from the bacterial strains JW/SL-YS485, a noticeable increase (49%) of biohydrogen production was achieved, and significantly increased by 900% after being deleted from strains M1442 [143,144]. The expression of HydA from *C. butyricum* was also reported to improve the biohydrogen yield by a factor of two [145,146] and increased by 20% after its overexpression in an isolated glycerol-consuming *E. coli* SS1 strain as compared with the environmental wild strains [145,147]. Therefore, manipulating the bacterial genetic codes is another promising way to strengthen the ability of bacterial cells to involve in the metabolic process leading to the enhancement of the biohydrogen yield from lignocellulosic agricultural residues.

4. Coupling dark fermentation and MEC strategy to enhance biohydrogen production

4.1. Agricultural straw biomass as feedstock for biohydrogen energy generation

Commonly, the used model substrate is glucose, but it is no longer preferable due to its high cost at present. Bartacek et al. have been suggested the criteria for a needed ideal substrate for large-scale renewable biohydrogen generation, that included minimum preliminary treatment demand, high carbohydrate content, renewable resources, freely available or at a low price, and high carbohydrate conversation efficiency via fermentation processes [148]. Those

substrates are further classed into four major categories, including pure substrates (such as acetate and glucose), solid wastes (e.g., food waste), energy crops (e.g. Miscanthus), and industrial wastewaters (e.g. wastewater). Most previously used substrates for biohydrogen production are summarized in SI.1.

Based on the fact that these lignocellulosic agricultural residues including straw biomass are rich in carbohydrates and freely available on the earth, Turner et al. suggested that they could serve as sustainable alternative feedstocks for H_2 production [149]. Agricultural straw biomass contain biodegradable organic compounds which can be converted to clean energy, and it is feasible for fermentative biohydrogen production, even though it requires pretreatment processes before use [150]. Therefore, using the agricultural straw wastes as feedstock for biohydrogen production is a promising sustainable application that could significantly contribute a lot to solid waste management and providing clean energy, that could replace fossil fuel-based energy and satisfy the global energy demands [151].

4.2. Dark fermentation for hydrogen production

Recently, the most common process for biohydrogen generation from agricultural straw wastes is dark fermentation (Fig. 5). The previously achieved biohydrogen yields from different agricultural residues feedstocks and the employed microbial cultures are summarized in Table 4. This process was performed by many researchers employing facultative (e.g., *Escherichia coli, Enterobacter aerogenes, Citrobacter intermedius,* and *Enterobacter cloacae* and obligate anaerobic bacteria such as *Clostridium cellulosi, Clostridium acetobutylicum, Clostridium tyrobutyricum, Clostridium beijerinckii, C. paraputrificum*, and *Ruminococcus albus*, etc.) [40,152–160].

The biohydrogen production through fermentative processes follows the anaerobic glycolytic breakdown of glucose (simple sugars). The indispensable metabolic pathway for converting agricultural straw biomass into pyruvate is glycolysis. Pyruvate, as the essential intermediate by-product, undergoes the acidogenic pathways and produces biohydrogen, and the yield depends on the type of the generated VFAs that include acetic acid, propionic acid, butyric acid, malic acid, and ethanol [161]. Obligate and facultative microorganisms utilize various organic substrates to produce biohydrogen [162]. The facultative anaerobic microorganisms use pyruvate formate-lyase to convert pyruvate to acetyl-CoA and formate and subsequently generate H_2 with formate H_2 lyase [142] (Fig. 4). Whereas, the obligate anaerobic microorganisms transform pyruvate to acetyl-CoA and CO_2 in the pyruvate

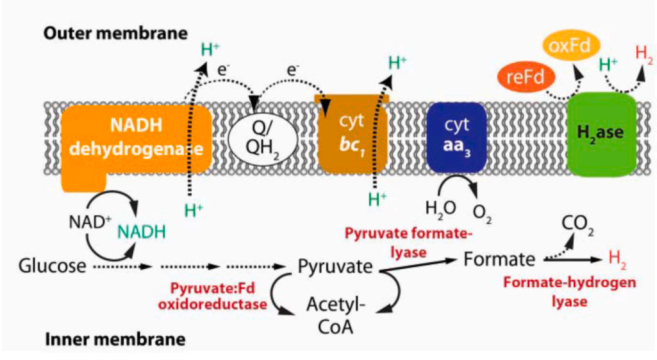

Fig. 5. Illustrating diagram of biohydrogen production via dark fermentation. (Adapted from Ref. [39] with permission of MDPI. Copyright 2015).

ferredoxin oxidoreductase-biocatalyzed processes, and the Fd reduction is required [163].

The production of biohydrogen gas is helped by the H^+ reducing mechanism during dark fermentation (see Fig. 5). The further decomposition of intermediates by-products takes place along with the feedstock degradation via dark fermentation, and it augments the reducing equivalents in microorganisms [164,165]. The enzyme NADH dehydrogenase catalyzes the liberation of H^+ from NADH/FADH, which is then reduced to hydrogen gas with the aid of hydrogenase together with the reduced Fd, while integral or peripheral protein structures (*such* as cytochrome *bc*1 and NADH dehydrogenase, and the mobile electron carriers (cytochrome *c* and quinone (Q)) facilitate the electron transport mechanisms via the Q pool (Fig. 5). Moreover, the further conversion between Q (QH_2) and H^+ transfers electrons to the cytochrome *bc*1 (cyt *bc*1) and the cytochrome *aa*3 (cyt *aa*3). As a result, the cyt *aa*3 reduces the Fe–S containing Fd, which liberates an electron to the hydrogenase involved in biohydrogen generation [142,165] (Fig. 5).

Generally, 12 mol of H_2 could be produced by complete oxidation of 1 mol of hexose to CO_2. However, under acetic acid fermentation, the theoretical H_2 yield cannot be higher than 4 mol which are typically lower. For one mole of hexose consumed, the biohydrogen yield is ranging from 1.0 to 2.5 mol. Under thermophilic dark fermentation, Varanasi et al. managed to produce 2.95 mol H_2/mol hexose using cellobiose as feedstock [166]. Note that, only 2 mol of the biohydrogen is produced when the butyric acid is the main fermentation intermediate product [150]. Furthermore, when the dark fermentation produces reduced organic compounds such as propionic acid, ethanol, and lactic acid, the biohydrogen yield become much lower because they are the dead-end by-products that couldn't further be converted to biohydrogen energy [167].

4.3. Microbial electrolysis cells (electrofermentation)

4.3.1. MEC description and working principles

Microbial electrolysis cells (MECs), also called electrofermentation or biocatalyzed electrolysis cells [187,188], is an emerging technology derived from microbial fuel cell (MFC) to produce biohydrogen through bio-electrochemical reactions (e.g., electrohydrogenesis process), where the proton is reduced at the cathode in waste treatment. In this technology, the anodic bacterial consortia oxidize the waste substrate and liberate protons, electrons, and carbon dioxide (Fig. 6) [1,189]. Subsequently, the generated electrons are then conveyed to the cathode electrode via the circuit wire, and the protons pass through the cation exchange membrane (CEM) or proton exchange membrane (PEM) to invade the cathode chamber where biohydrogen is generated, as shown in Fig. 6 [1,189,190]. However, for this process to occur, it requires at least −0.414 V of voltage at the cathode [1,191]. Compared to normal fermentative biohydrogen production, MEC technology requires low energy input and drives nearly all stoichiometric conversation of the feedstock to biohydrogen while dark fermentation achieved only 33% [189,192–196]. The electrohydrogenesis efficiencies depend on the used electrode materials, applied potential range, type of microorganisms, type of the used membrane, design of the MEC reactors, and remarkably affected by the feedstock types. High biohydrogen yield and energy efficiency were reported for readily biodegradable substrates. The biohydrogen production in MECs using acetate as an electron donor is demonstrated in equations (1) and (2) under 25 °C, pH = 7.0, and 1 atm) [191].

$$\text{Anode: } CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H+ \quad (1)$$

$$\text{Cathode: } 8H+ + 8e^- \rightarrow 4H_2 \quad (2)$$

Table 4
The achieved fermentative biohydrogen yields from various lignocellulosic agricultural straw biomass under different microbial cultures (Adapted from Ref. [1] with permission of Springer Nature. Copyright 2018).

Substrate type	Microbial inoculum source	Reactor type	Temperature (°C)	pH	Highest H_2 yield/rate	H_2 fraction (%)	References
Cornstalk waste	Anaerobic sludge	Batch	50	7.0	141.29[a]	57.85	[168]
Soybean straw	*Clostridium butyricum*	CSTR	35	7.0	60.2[a]	–	[169]
Miscanthus biomass	*Clostridium beijerinckii* NCIMB 8052 and *Geobacter metallireducens* GS-15	Batch	30	5.5	1.67 ± 0.14 mmol H_2 L^{-1} h^{-1}	–	[170]
Fruit waste	Anaerobic mixed sludge	CSTR	55	5.0	513[a]	–	[171]
Sugarcane leaves	Anaerobic mixed sludge	Batch	37	6.15	248.05[b]	26.73	[172]
Waste sorghum	Anaerobic mixed sludge	Batch	37.5	7.0	213.14[b]	43.75	[173]
Dairy solid cow waste	Anaerobic mixed sludge	CSTR	37	5.5	150.59 ± 35.70 mL H_2 L^{-1} day^{-1}	41.01 ± 2.57	[174]
Brewery wastewater	*Rhodobacter sphaeroides* NCIMB 8253	Batch	30	7.0	0.69[b]	–	[175]
Bread waste	*Rhodopseudomonas palustris* 42OL	Batch	25–28	6.8	3.1[b]	–	[176]
Food industry waste	Anaerobic sludge	CSTR	35	5–5.9	101.75 ± 3.71[a]	46–54	[177]
Rice straw	*Thermoanaerobacterium thermosaccharolyticum* M18	Batch	60	7.0	22.08 mmol H_2 L^{-1}	–	[178]
Sugarcane bagasse	*Thermoanaerobacterium thermosaccharolyticum*	Batch	50	7.0	6.2 L H_2 L^{-1}	–	[179]
Fruit and vegetable waste	Anaerobic sludge	Batch	55	7.0	31–76[a]	–	[180]
Coconut husk	*Enterobacter aerogenes* NBRC 13534	Batch	37	7.0	0.279[b]	–	[181]
Sugarcane vinasse and cheese whey	Anaerobic mixed sludge	AFBR	55	7.06	1.01 ± 0.06 mmol H_2 g^{-1} COD	47.3 ± 2.9%	[182]
Fruit and vegetable waste	*Thermotoga maritima* DSM 3109	Batch	80	7.0	3.46[b]	–	[183]
Potato waste	Anaerobic sludge	CSTR	35	5.5	150[a]	42.5–46.33	[184]
Bean waste	Anaerobic sludge	CSTR	35	5.5	80[a]	44–52.3	[184]
Sweet sorghum stover hydrolysate	*Trichoderma asperellum* BPLMBT1	Batch	37	7.0	402.01 mL H_2	–	[185]
Palm oil mill effluent (POME)	POME sludge	Batch	50	5.5	28.47[a]	–	[186]

–, Data not available.
[a] mL H_2 g^{-1} substrate $_{removed.}$
[b] mol H_2 g^{-1} mol glucose.

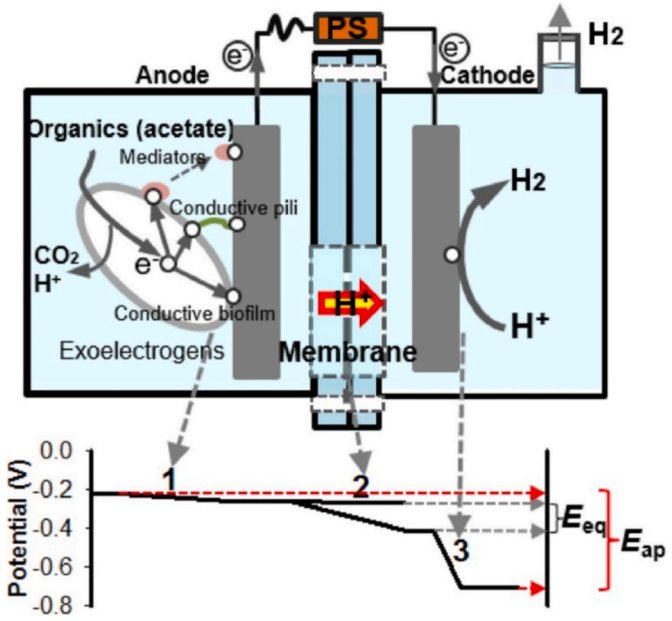

Fig. 6. Illustrating diagram of electrohydrogenesis in MEC operated with acetate as a model electron donor and its possible voltage losses. Anodic potential losses (1); Membrane and ohmic losses (2); and Cathodic potential losses (3). (Adapted from Ref. [194] with permission of Elsevier Ltd. copyright 2017).

4.3.2. Bio-electrochemical dynamics in MEC for electrohydrogenesis

Dark fermentation has been approved by many researchers as an alternative strategy for biohydrogen production using renewable biomass and wastewaters [194], however, the biohydrogen yield was quite low, owing to the excessive generation of the aforementioned non-fermentative organics [194]. The further conversation of those dead-end by-products (e.g. acetic acid) to biohydrogen energy could not be done by microorganisms without additional energy supply ($CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + H^+ + 4H_2$, $\Delta G^0 = +104.6$ kJ reaction^{-1}) [187,194,197]. For instance, only 4 mol H_2 and 2 mol H_2 are produced per 1 mol of glucose when the end-fermentative products are acetate and butyrate respectively regardless of its stoichiometric potential of 12 mol H_2 per 1 mol of glucose [194,197,198].

The electrohydrogenesis process has been proved to eliminate the endothermic barrier for biohydrogen promotion by supplying the required extra energy. In this process, the added small external energy together with that produced by anode respiring bacteria (ARB) facilitate the transfer of the generated electrons to the cathode, where they react with protons and generate additional biohydrogen gas to the produced one from fermentative processes, thus enhance the biohydrogen energy evolution.

If we take acetate as a model example, the anodic reactions occur following equation (3) [191,194].

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad (3)$$

The theoretical anode electrode potential (Ean) for the oxidation of acetate under biological standards conditions [190,194], (Temperature (T) = 298.15 K; pH = ~7.0; $[CH_3COO^-] = 0.0169$ mol L^{-1}; and $[HCO_3^-] = 0.005$ mol L^{-1}, is calculated as follow on the basis of the Nernst Equation (4)

$$E_{an} = E^{o}_{an} - \frac{RT}{8F} ln \frac{[CH_3COO^-]}{[HCO_3^-]^2[H^+]^9} \Leftrightarrow 0.187 - \frac{8.31 \times 298.15}{8 \times (9.65 \times 10^4)} \ln \frac{[0.0169]}{[0.005]^2[10^{-7}]^9} = -0.3V \quad (4)$$

where E^0_{an} represents the standard electrode potential (~0.187 V), R stands for the ideal gas constant (8.31 J mol^{-1} K^{-1}), F is representing Faraday's constant (9.65 × 10^4 C mol^{-1}), and T stands for the temperature in Kevin (K). The H_2 production at the cathode electrode is achieved through the following H_2 generating equation (5) [188,194]; and under T = 298.15 K, pH = 7.0, and P_{H2} = 1 atm, the theoretical cathode potential is calculated following the below equation (6):

$$2H^+ + 2e^- \rightarrow H_2\ (g) \quad (5)$$

$$E_{cat} = E^{o}_{cat} - \frac{RT}{8F} ln \frac{P_{H2}}{[H^+]^2} \Leftrightarrow 0 - \frac{8.31 \times 298.15}{8 \times (9.65 \times 10^4)} \ln \frac{1}{[10^{-7}]^2} = -0.414V \quad (6)$$

where E^0_{cat} stands for a standard electrode for H_2 evolution (0 V); whereas P_{H2} is representing H_2 partial pressure (1 atm). Hence, the equilibrium voltage is given by the following equation (7) [194].

$$E_{eq} = E_{cat} - E_{an} = (-0.414) - (-0.300) = -0.114V \quad (7)$$

The negative Eeq indicates that further conversation of left acetate amount to biohydrogen is not spontaneous (Equation: 7). Therefore, the thermodynamic limitations do not allow dark fermentation to be considered as a promising approach for biohydrogen production from lignocellulosic agricultural residues [194]. To alleviate that thermodynamic barrier and promote biohydrogen production, an additional voltage input of >0.114 V is required in the process named electrohydrogenesis (microbial electrolysis processes). For practical aspects, applying a voltage (E_{ap}) of 0.2–0.8 V is recommended, because it would be larger than Eeq owing to the energy especially from ohmic losses, microbial metabolic losses, activation losses, and transport losses [32,194,199]. For instance, Rozendal et al. investigated the possibility of producing biohydrogen from sodium acetate and applied 0.5 V to recover 0.02 m^3 H_2/m^3 -reactor volume per day, and also reported at the anode 0.04 V of voltage loss, 0.01 V as the outcome of the membrane and ohmic resistance, whereas the voltage was >0.28 V at the cathode [192] (Fig. 6). However, compared to the voltage needed for water splitting (1.23 V), the applied one for electrohydrogenesis processes (MEC) is much lower [193,194].

4.3.3. Dark fermentation combined with microbial electrolysis cells accelerates agricultural straw biomass degradation and enhances hydrogen yield recovery

The commonly employed methods (such as steam reforming of hydrocarbons, autothermal reforming, and non-catalytic partial oxidation of fossil fuels) to generate hydrogen are high energy-consuming processes (>850 °C), not environmentally friendly, and not cost-effective [189]. Therefore, the biological pathways that don't require intense energy to produce hydrogen from agricultural wastes as feedstock under environmental standard conditions would be more preferable than those most conventional used ones [189]. Many investigators have categorized the biological methods that generate biohydrogen from agricultural residues into two main groups which are light-dependent processes (including photo-fermentation, direct and indirect biophotolysis) and the light-independent methods which include dark fermentative processes and microbial electrolysis process [200]. A detailed discussion about the main reactions, the advantages, and disadvantages of each process is summarized in Table 5. Compared to light-dependent methods, the dark fermentative process produces higher biohydrogen yield and has high potentials of degrading the used carbon source (lignocellulosic agricultural residues) [35], however, the biohydrogen yield has remained dissatisfactory [201]. Therefore, a sustainable strategy to improve the biohydrogen recovery from straw biomass was in an emergency needs to be developed. On the other hand, the bioelectrohydrogenesis was reported as a promising process for promoting biohydrogen generation based on its high substrate conversion capacity (90–100%) [202], and this novel technique has successfully converted lignocellulose straw biomass into biohydrogen gas with improved yields [203,204].

Integrating microbial electrohydrogenesis and dark fermentative processes could strongly promote agricultural straw biomass biodegradation, thereby enhance biohydrogen yield [217]. [34,35,203,204,217]. This two-stage strategy, its first stage (DF) is responsible for converting carbohydrates-rich substate (e.g., agricultural residues) into biohydrogen, CO_2, VFAs, and alcohols using various microorganisms, and the resulting fermentation effluent is then used as feedstock in the second stage of electrohydrogenesis via microbial electrolysis cells (MEC) to produce supplemental biohydrogen energy (Fig. 7) [34,218–220].

The applied external voltage on MEC has the potential to overcome the thermodynamic limitation during the fermentation biohydrogen production, and further produce the biohydrogen from the fermentative dead-end products that couldn't be converted with DF alone. Besides, the dark fermentation stability and effectiveness are also promoted by its integration with MEC [34]. MEC-DF system favors the formation of microbial diversity and the robust bacterial biofilm with a thick peptidoglycan cell wall that gives them the capacity of resisting the external environmental disturbances, which thus accelerate the substrate decomposition for enhanced biohydrogen evolution. Various bacterial species such as electrogenic bacteria and exoelectrogenic bacteria showed improved growth in the MEC-DF system significantly promoted substrate decomposition. For instance, the *Geobacter* species, the most popular exoelectrogens in MEC-DF has shown the ability to convert different organic maters including the fermentative byproducts (VFAs, and alcohol) into biohydrogen [34,221]. Some other microbial populations *Smithella* sp., along with *Geobacter sulfurreducens* known for their potential to degrade propionate were also abundantly found in MEC-DF [34]. *Clostridium* and *Bifidobacterium* which convert complex organic wastes into biohydrogen were also found abundant in MEC-DF than the control system as well [34]. Hence, the optimum supplied voltage on the MEC system favors the dominance of electroactive bacterial species in the bacterial inoculum and promotes the existence of microorganisms responsible for agricultural residue degradation. Therefore, applying a voltage potential in MEC-DF is imperative for achieving high rates of lignocellulosic agricultural residues decomposition, substantial biohydrogen production, and high energy efficiency.

This research area is still new for biohydrogen production; therefore, they are a scarcity of works on biohydrogen production using the MEC-DF integrated system. Nevertheless, the few studies displayed promising results. For example, Laurette et al. achieved a noticeable yield of 9.9 mol H_2/mol glucose, which corresponded to 80% of the total yield in the MEC-DF system [222], and also observed a remarkable biohydrogen yield increment from 1.64 to 9.95 mol H_2/mol of glucose in a sequential batch process of DF and MEC system [222]. Likewise, with MEC-DF integrated system, 94.2 L H_2/kg VS was achieved using wastewater from cheese whey as feedstock [223]. MEC-DF integrated system has also achieved biohydrogen yield from corn stover, fourfold higher than dark fermentation has achieved, which indicates that the application of this technology increases the biodegradation of lignocellulosic biomass rate and promote biohydrogen production [203]. Furthermore, Wang

Table 5
A detailed summary of biohydrogen-producing methods from organic wastes. Described the main differences, occurred reactions, advantages, and disadvantages of each biological and thermochemical method.

Methods	Definition	Main reactions	Advantages	Disadvantages	References
Direct biophotolysis	It's the process that breaks down the molecules of water into hydrogen and oxygen in presence of light by photoautotrophic microalgae.	$2H_2O + light \rightarrow 2H_2 + O_2$	• Cost-effective process • Uses only water and sunlight to generate H_2 • Significant increase in energy conversation compared to other biomass (trees or crops).	• The high light intensity needs. • Concurrently generation of H_2 and O_2 and the latter negatively affects the whole system. • Lower photochemical efficiency	[205]
Indirect biophotolysis	This process generates hydrogen from water via algal or blue-green algae photosynthetic system by converting solar energy into chemical energy which is hydrogen. It involves two processes: the first is the production of the biomass through photosynthesis reactions, and the second is the utilization of that biomass for hydrogen production via dark fermentation process.	(a) $6H_2O + 6CO_2 + light \rightarrow C_6H_{12}O_6 + 6O_2$ (b) $C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$ (c) $2CH_3COOH + 4H_2O + light \rightarrow 8H_2 + 4CO_2$ Overall reaction $12H_2O + light \rightarrow 12H_2 + 6O_2$	• The blue-green algae produce hydrogen by using water • The fixation of nitrogen gas from the atmosphere	• Needs of the removal of some hydrogenase enzymes to stop the degradation of H_2. • 30% of the produced gas is oxygen	[200,206]
Photo-fermentation	This process refers to the fermentative conversion of organic substrate to hydrogen by employing photosynthetic microorganisms via biochemical reactions which includes three steps similar to anaerobic conversion.	$CH_3COOH + 2H_2O + light \rightarrow 4H_2 + 2CO_2$	• The employed bacteria can use a wide spectral light energy • Suitable to various types of organic wastes. • High conversion efficiencies of the substrate.	• Slow production rate of H_2 • The produced O_2 inhibits the nitrogenase, • The pretreatment requirements of the substrate. • Hight implementation costs.	[200,206]
Dark fermentation	It is described as the fermentative conversion of the organic substrate to biohydrogen by microorganisms in the absence of light.	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$	• It's a simple and cost-effective process • Achieved high H_2 production rate • Capacity to generate H_2 without light • The utilization of different kinds of substrates	• O_2 can inhibit the hydrogenase • Achieve lower biohydrogen yield • The augmentation of H_2 pressure turn the process thermodynamically unfavorable • The separation of H_2 from the produced gas, CO_2 is needed.	[200,206]
Microbial electrolysis	Microbial conversation of the organic material to hydrogen and methane by applying an electric current.	$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2CH_3COOH$ Anode: $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$ Cathode: $8H^+ + 8e^- \rightarrow 4H_2$	• Generation of biohydrogen directly from waste streams • Effective and promising future approach to hydrogen generation from lignocellulosic agricultural residues	• To date, the involved metabolic pathways are still well known • Low production of the H_2 when the electrode power densities are low • Energy efficiency is negatively influenced by a high applied voltage	[207,208]
Thermochemical gasification	It is defined as the partial oxidation of biomass to produce a synthesis gas (syngas). The steam gasification enables thermal treatment under a reducing atmosphere that thus promotes the H2 generation.	$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 +$ other species **Water-gas shift reaction** $CO + H_2O \rightarrow CO_2 + H_2$ (+small amount of heat)	• Achieve maximum conversion of the substrate to biohydrogen.	• The requirements of the special conditions of gas maintaining • Tar removal	[209,210]
Pyrolysis	Pyrolysis is the process that decomposes the organic wastes to generate hydrogen-rich gas at high temperatures. The operating process doesn't involve any other oxidizing or reactant agents	NA	• Generation of other inhibitors byproduct along with bio-fuel • Chemicals and minerals	• Eventual deactivation of the catalysts	[210–212]
Solar gasification	Solar gasification is also defined as the thermochemical conversation of organic matter (biomass) into high-value syngas by employing concentrated solar energy as the heat source for driving reactions.	NA	• Produces and increases good H_2 yield • Increases the energy conversion efficiency at lower temperatures • No need for partial combustion • Crushing or grinding the substrate is not needed before entering the operating reactor • Ash and tar can be easily removed • Generate a very little amount of CO_2	•High cost of the effective collector plates	[213,214]

(*continued on next page*)

Table 5 (*continued*)

Methods	Definition	Main reactions	Advantages	Disadvantages	References
Supercritical conversion	Supercritical water gasification is a thermochemical hydrogen generation process that involves the employment of supercritical water (water above its critical point of 374.1 ^{O}C and 22.1 MPa) as the gasifying agent.	$2C_6H_{12}O_6 + 7H_2O \rightarrow 9\ CO_2 + 2\ CH_4 + CO + 15H_2$	• Continuous process able to operate at night • High hydrogen content • Doesn't need to dry the substrate • High gasification efficiency and H_2 selectivity • Development of clean gaseous products • Generation small amounts of tars and chars.	• Requirements of the supercritical medium selection	[215, 216].

NA = not available.

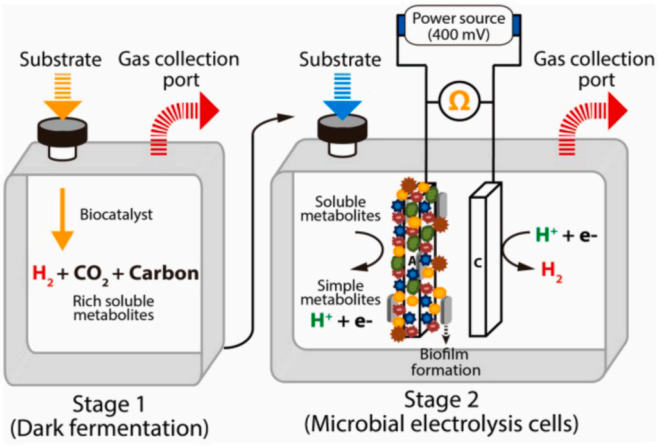

Fig. 7. A schematic diagram of a MEC and DF coupled system for biohydrogen yield promotion. (A: Anode; C: Cathode; Brown, orange, blue and Green symbols in the biofilm stand for electrochemically active mixed microbial population). Actually, in stage 1, lignocellulosic agricultural wastes (straw) are employed for dark fermentative biohydrogen production, and the remaining acid-rich effluents become the feedstock for electrohydrogenesis for further promotion of biohydrogen generation. (Adapted from Ref. [39] with permission of MDPI. copyright 2015).

et al. achieved twofold hydrogen production from 0.24 L/L per day in fermentation processes to 0.48 L/L per day in an integrated system of MEC and DF [224], and also biohydrogen production augmented when employing corn stalk as a carbon source in the same system [225]. Meanwhile, Wang et al. again combined two systems (DF and MEC) using cellulose as substrate and achieved an enhanced biohydrogen yield which was approximately 42% higher than in DF [224].

The biohydrogen production cost through MEC-DF integrated system was also reviewed and compared the findings with another hydrogen electrolytic production coast. The national renewable energy laboratory (NREL), reported that the fermentative biohydrogen production cost from lignocellulosic agricultural residues was \$4.33/kg H_2 [204], whereas, in the microbial assisted-electrolysis system alone, the production cost was \$12.43/kg H_2 with the enhanced hydrogen yield which was 2.4folds that from DF alone [204]. Though the biohydrogen cost was high for the latter, it has significantly reduced to \$6.61/kg H_2 after integrating the MEC and DF system which was comparable with that of the electrolytic hydrogen cost of \$ 4.6/kg H_2 [226], and even much lower than that reported by Shaner et al. who estimated the hydrogen production cost of \$12.1/kg H_2 with photovoltaic-electrolytic solar--hydrogen production method [204,226,227]. Therefore, the integration system we are encouraging, if it could successfully be matured, cost-optimized it could be far more economical than other electrolytic hydrogen production methods, which could make it a most promising sustainable application to produce renewable clean energy (biohydrogen) to replace fossil fuel-based ones. The previously published works on the production of biohydrogen from lignocellulosic agricultural residues and other complex substrates by coupling dark fermentation and microbial electrolysis are summarized in Table 6.

5. Operational parameters affecting H_2 production

The MEC and dark fermentative biohydrogen production from agricultural residues is a very complex process governed by many factors that include inoculum, temperature, nutrients (Nitrogen, phosphate, metal ions), hydraulic retention time, hydrogen partial pressure, pH, alkalinity, fermentation end-products, and lignocellulosic biomass pretreatment-linked inhibitors. Though the effects of alkalinity on biohydrogen production seem to be less investigated, the rest factors have been previously well studied, and are thoroughly discussed below in this review. The biohydrogen production process is discussed in section 4.2.

5.1. Inoculum

As aforementioned in section 5.2, the fermentative bacteria are categorized into three main groups including strict anaerobic bacteria [40,41,157], facultative anaerobes [40,41,156,158,159], and aerobic bacteria such as *Bacillus* [40,41,160]. The facultative anaerobic bacteria produce up to 2 mol of H_2/mol glucose, whereas the strict anaerobes (*Clostridia*) produce 4 mol H_2/mol glucose [40,41,231]. In recent studies, *Clostridium* sp. was employed as inoculum and generated 1.61–2.36 mol $H_2.mol^{-1}$ glucose, and *Bacillus licheniformis* produced 0.37 and 1.1 mol H_2/mol glucose in semi-continuous and batch mode, respectively [41,148]. The hydrogen yield of 1.9, 1.2, and 5.6 mol H_2/mol L-arabinose, xylose, and cellobiose were respectively achieved by employing *Bacillus coagulants* during the dark fermentation process [41,232]. The strict anaerobic bacteria are so sensitive to oxygen and a small amount is enough to stop the hydrogen-producing activities. Therefore, the facultative anaerobes are more cost-effective for biohydrogen production since they can consume very fast oxygen and keep the anaerobic environment condition [40,41]. The source of these hydrogen-producing bacteria is from pure culture or mixed culture (especially from anaerobic sludge, organic compost, soil, urban solid wastes, and bovine manure) [41,231]. The mixed culture holds many advantageous features over the pure culture for biohydrogen production such as low operational costs, cosmopolite source, and simplicity of operation, and easy control, whereas the pure culture is highly susceptible to contaminants. Therefore, the mixed culture is more suitable for large-scale industrial applications to produce biohydrogen from lignocellulosic agricultural residues. The only challenge for using the mixed culture is the involvement of the hydrogen-consuming bacteria, which makes the requirement of the pretreatment of the culture; to inactivate the hydrogen-consuming bacteria and activate the hydrogen-generators [40,231,233]. The inoculum source and related pretreatment strategy were reported to affect the biohydrogen production from lignocellulosic agricultural residues [40]. The main reason behind the mixed anaerobic

Table 6
Collection of recent works that produced biohydrogen from different recalcitrant substrates by combining dark fermentation and bioelectrohydrogenesis (Adapted from Ref. [228] with permission of Elsevier Ltd. copyright 2017).

Substrate source	Type of DF reactor	Electrodes' materials used in the ME stage		Applied volt. (V)	YH_2 DF-I stage (mLH_2/gCOD)	YH_2 ME-II stage (mLH_2/gCOD)	YH_2 coupling (mLH_2/gCOD)	Electric efficiency (Wh/mol H_2)	COD removal (%)	Ref.
		Anode	Cathode							
Domestic wastewater	Batch 35 °C	Graphite brush	Carbon cloth with a Pt catalyst layer.	0.8	135.15*	1200.00	1335.15*	51.56*	50	[229]
Cellulose	CSTR 60 °C	Brush carbon fibers	Carbon cloth with a Pt catalyst layer	0.44	57.58*	812.72*	870.30*	78.91*	15	[224]
Cornstalk	Batch 36 °C	Two pieces of square graphite felts	Carbon cloth with a Pt catalyst layer	0.8	168.16*	1000.00	1168.16*	47.83*	44 ± 2	[225]
Crude glycerol	Batch 35 °C	Heat-treated graphite brush	Carbon cloth with stainless steel mesh	1.0	124.10*	106.15	230.25*	NA	10.4 ± 1.4/ 40.6 ± 4.9%	[230]
Lignocellulose and cellobiose	Batch 50 °C	Graphite fiber brush pretreated using an NH_3	Flat carbon cloth containing a Pt catalyst	0.5	225.92*	900.00	1125.92*	36.09*	50	[222]
Ricotta cheese whey (CW)	Batch 37 °C	Carbon felt	90% Platinum-10% Iridium mesh	0.2	122.27	714.69	836.96	18.12	78.5 ± 5.7	[228]
Fruit juice production wastewater (FJW)	Batch 37 °C	Carbon felt	90% Platinum-10% Iridium mesh	0.2	130.41	1478.22	1608.63	10.95	71.8 ± 1.6	[228]
Fruit processing wastewater (FPW)	Batch 37 °C	Carbon felt	90% Platinum-10% Iridium mesh	0.2	101.85	652.42	754.27	21.50	73.8 ± 3.6	[228]
Papermill wastewater (PW)	Batch 37 °C	Carbon felt	90% Platinum-10% Iridium mesh	0.2	37.37	219.39	256.76	23.26	57.1 ± 6.1	[228]
Sugar production wastewater (SW)	Batch 37 °C	Carbon felt	90% Platinum-10% Iridium mesh	0.2	51.91	344.33	396.24	25.16	67.0 ± 13.1	[228]
Vinasse from spirits production (VB2)	Batch 37 °C	Carbon felt	90% Platinum-10% Iridium mesh	0.2	87.70	1399.57	1487.27	18.37	47.3 ± 6.4	[228]

YH_2 = Hydrogen yield; DF = dark fermentation; ME = microbial electrolysis; * = Calculated; NA = not available.

culture pretreatment prior to MEC-dark fermentative hydrogen production is to inhibit the methanogenic metabolic activities and favor the biohydrogen-producing bacterial growth as discussed in section 5.3.4.

5.2. pH

pH is an important factor for hydrogen-producing bacterial growth and controls the redox conditions for fermentative biohydrogen production processes since it affects the enzymatic activities and metabolic transport [234–236]. Changing environmental pH values conspicuously alters the metabolic reactions within the hydrogen-producing bacterial cell and thus modify the pH-dependent fermentations linked with biohydrogen generation [237]. For instance, pyruvate is converted to VFAs in the acidic environment (low pH), produces CH_4 by methanogens in a neutral pH [165], and the H_2-producing microorganisms are metabolically more active at pH = ~6.0 [238]. The acidic environment with a pH under 4.5, was reported harmful to H_2 producing bacterial population, thus hinders the H_2 production [40,136,236,237]. The low pH deactivates the enzyme (Fe–Fe) hydrogenase activity and thus impedes biohydrogen production [239–241]. Also, the low pH promotes the generation of protons from the decomposition of the organic acids, and those ions invade hydrogen-producing bacterial cytoplasm and inhibit their normal growth [241]. The alkaline condition was reported to do not favor biohydrogen-fermentative processes to solventogenesis [242] since a higher initial pH promotes ethanol and propionate production [40,41,231]. During dark fermentation and electrofermentation processes, the optimum pH for both biohydrogen production and the prevention of methanogenesis and solventogenesis varies from 5.5 to 6.5 [241,242]. At pH 5.5, the highest achieved biohydrogen yield was 117.24 mL/g sugar from rice bran as feedstock, and the highest achieved volume of hydrogen was at pH 6.5 [41,231]. The recent study also reported the highest biohydrogen production of 509.2 mL/g sugar from a wheat straw as a source of carbon at pH 6.5 [40,41].

5.3. Alkalinity

Alkalinity always refers to buffer capacity in the fermentative process, which is described as the equilibrium of CO_2 and bicarbonate ions that deliver substantial resistance to sudden changes in pH. The dysfunctioning feature of the fermentative digester could be investigated by considered the internal buffer capacity instead of looking at pH measurement perspectives [122]. It has been reported that bicarbonate alkalinity (BA) can decrease the fluctuation of the large pH in fermentative biohydrogen production [122,243,244]. The high BA in the dark fermentation broth, augments the carbon dioxide concentration within the bioreactors, which thus predict the possible consumption of biohydrogen via the homoacetogenesis process [243,245]; however, the low alkalinity within the bioreactor, was reported to promote hydrogen production. For example, in 2015, Jeongdong et all., produced a maximum hydrogen yield of 1.5 mol H_2/mol glucose (at pH 6 & 7) with low alkalinity in the fermentation broth (BA: <0.1 g $CaCO_3$/L). However, with the high alkalinity (BA of ~2.5 g $CaCO_3$/L), they produced only 1.08 mol H2/mol glucose at pH 8 & 9 conditions and detected no hydrogen yield at higher than 3.0 g $CaCO_3$/L (BA) [243]. The excessive incorporation of the alkali-rich compounds and high amount of BA were reported so harmful to biohydrogen-generating bacteria, which results

in decreasing biohydrogen yield [122,243,244,246]. Therefore, the control of alkalinity during MEC-DF operations is a key factor for enhanced biohydrogen production.

5.4. Temperature

Temperature is an essential operating factor during dark fermentation and electrohydrogenesis because the changes in the temperature noticeably affect agricultural residues utilization, influence the biohydrogen-generating bacterial growth which subsequently affects MEC-dark fermentative biohydrogen generation and the related intermediate by-products formation. Increasing temperature enhance the metabolic activities of the bacteria that govern the biohydrogen producing processes, but the excessive increase at high extends was reported to impede the hydrogen-producing bacterial metabolic activities, which results in decreasing the biohydrogen production [20,241,247].

Many investigators, have reported that dark fermentative biohydrogen production is possible at various temperature ranges including ambient (15–30 °C), mesophilic (30–45 °C), thermophilic (50–60 °C), and extremely thermophilic or hyper-thermophilic (>60 °C) [41,167,241,248]. However, the optimal temperature for biohydrogen production in a mixed culture varied according to the best growth temperature conditions for each species [150,167,249]. Mesophilic bacteria were commonly used in biohydrogen production experimental works due to their rapid and maximum growth rate [250]. However, it also promotes hydrogen-consuming bacterial growth as well [241]. It has previously reported that using a mixed microbial population and increase the temperature from 35 to 45 °C, the achieved maximum biohydrogen production of ~319 mL of H_2/g feedstock, and significantly dropped to ~182 mL of H_2/g feedstock with a further increase of temperature from 45 to 55 °C [249]. The results of Lin et al. also indicated that the optimum temperature of 45 °C achieved the highest biohydrogen yield when using a mixed culture in a chemostat-type H_2 bioreactor [251].

Referring to the lignocellulosic agricultural residues as feedstock, the mesophilic bacteria were reported to do not have the ability to convert cellulose directly into biohydrogen, the commercial cellulase enzyme is needed to be incorporated into the system to catalyze the bacterial hydrolysis. However, the thermophilic anaerobic bacterial community effectively hydrolysis and convert cellulose into biohydrogen without the inclusion of the exogenous cellulase [241]. The feedstock conversation rate was reported high in thermophilic conditions [38,241]. Several published studies showed that thermophilic and hyper-thermophilic bacterial consortia produce more hydrogen yield than mesophilic consortia [241,252]. Indeed, performing MEC-dark fermentative biohydrogen production at high temperatures displayed lots of advantages such as the better mixing of the fermentation effluent, less risk of contamination, lower viscosity of the fermentation broth, and higher reaction rates. Moreover, when employing straw biomass as a substrate, the thermophile achieved a maximum biohydrogen yield of ~4 mol H_2/mol, approximately twofold that of mesophilic-used processes [252]. Notably, the thermophile-used processes are thermodynamically favorable for promoting biohydrogen production because it increases the system's entropy, and thereby becomes more energetic, and thus stimulate the H_2-processing enzymes and bacterial consortia [249].

5.5. Nutrients

Nutrients are also an indispensable parameter for biohydrogen-producing microorganism growth. It has been reported that the C/N ratio affects both bacterial growth and biohydrogen generation for mixed fermentative consortia or pure cultures [253]. The biohydrogen yield of ~4.8 mol H_2/mole of sucrose and the production rate of ~270 mmol H_2/L per day were achieved at a C/N ratio of ~47 [245]. During fermentative processes operated with a mixed culture, with 0.1 g of N/L, Wang et al. obtained a maximum biohydrogen production and H_2 yield of (291.4 mL) approximately ~3.25 mmol and ~3.33 mmol H_2/g of glucose respectively [254]. Nevertheless, a high concentration of nitrogen remarkably influence the intracellular pH of the microbial population involved in biohydrogen production and impede the nitrogenase activity [255,256], and it has been proved that the excess amount of N induced ammonification reactions which don't favor the biohydrogen production [257].

Phosphate is also a key inorganic nutrient that participates actively in biohydrogen production during dark fermentation and electrohydrogenesis reactions, therefore its optimum concentration is taken as an essential factor to promote the biohydrogen yield [245]. Moreover, adenosine triphosphate (ATP) facilitates cellular energy production, and it takes part in controlling the buffering capacity as a substitute for carbonate [164]. However, an excess amount of phosphate induces extravagant VFAs generation, which considerably decreases the biohydrogen yield. Note that, most of the dark fermentation processes, need additional metal ions to stimulate enzymes and co-enzymes related to microbial metabolism for bacterial growth [258]. The most-reported enzyme with a huge contribution to biohydrogen production is hydrogenase [259], and iron (Fe) that facilitates the electrons transfer to hydrogenase because it is considered as the active site for Fd. It has been shown that the high concentrations of Fe could positively affect biohydrogen production because it is a key element of the Fd and hydrogenase [260–262]. Investigators indicated that the best amount of Fe to achieve better results, should vary from ~25 up to 100 mg/l, and beyond that level, it could induce toxicity [263]. The effects of trace elements such as Zn, Co, Mo, Mn, Ni, K, Fe, I, Mg, Cu, Ca, and Na for biohydrogen production from agricultural residues were also investigated, and researchers reported that their concentrations should be controlled as well for high biohydrogen production [258,261,264].

5.6. Hydraulic retention time

This index is so essential in the selection process of microbial population that could effectively involve in MEC-dark fermentative biohydrogen production and tolerate mechanical dilution created by the continuous volumetric circulation within the reactors. It has been reported that increasing Hydraulic Retention Time (HRT) favors the metabolic activities of H2-producing bacteria which thus enhances biohydrogen production in a MEC-DF integrated system, however, the continuous increase far beyond the optimum levels resulted in decreasing the hydrogen yield [20]. A short HRT delays the methanogens growth rate and maintaining it at 2–10 h which effectively suppresses all methanogenesis processes which results in favoring the biohydrogen production from lignocellulosic agricultural residues [265]. However, the elongated dark fermentation shifts acidogenesis processes to methanogenesis thus inhibits biohydrogen production [155]. Many researchers reported that the optimum HRT that favors biohydrogen production varies from 8 to 14 h for different types of feedstocks including lignocellulosic agricultural biomass [137,155,266]. However, it is affected by several parameters that include the organic loading rate, the type, and composition of the substrate, the system redox condition, and the type of microorganism, etc.

5.7. Hydrogen partial pressure

Hydrogen partial pressure (HPP) is referred to the amount of biohydrogen gas that could be generated within the reactor during the MEC-dark fermentative biohydrogen production [241]. It is an important rate-limiting parameter for biohydrogen generation in MEC-dark fermentation processes, in its excess, it intends to decrease hydrogenase activity through the negative feedback inhibition [150,241]. The augmentation of the dissolved biohydrogen in the fermentation broth favors the reduction of oxidized ferredoxin (Fd) and thereby causes the reversible oxidation of hydrogenase and the reduction of Fd, which thus impede biohydrogen production due to the oxidation of dissolved H_2

[241].

Under high HPP situations (≥60 Pa), the acidogenesis process shifts to solventogenesis to produce reduced products such as alcohol that can't be further fermented without additional energy, and thereby decrease biohydrogen yield [267]. In this case, the electrohydrogenesis process provides that supplemental energy to enhance the conversion of those reduced products into additional biohydrogen. The conventional reported HPP that favors the biohydrogen production in the MEC-DF system is 0.5 atm at 60 °C, 0.2 atm at 70 °C, and 0.02 atm at 98 °C [241,268]. Different researchers have indicated that sparging N_2 and Argon (Ar) into the operating bioreactor headspace together with gas stripping to keep low Partial Pressure of Hydrogen, has fortunately enhanced the biohydrogen production from agricultural residues by 68% [242,269]. Hence, the reactors should be operated at a low HPP to promote biohydrogen production from lignocellulosic agricultural biomass via the MEC-DF strategy [150,242,270].

5.8. Fermentation end-products

The fermentative biohydrogen production is inevitably accompanied by various organic acids as end-products, which substantially decrease the pH of the operating reactor and thereby inhibit the hydrogen-producing bacterial growth [40]. In most of the cases, the fermentation effluent composition is mainly 137–3480 mg/L, 119–5780 mg/L, and 160–1920 mg/L for acetic, butyric, and butyric acid respectively [40,271]. However, it contains some other end-product in small proportions which include ethanol (31–634 mg/L), butanol (35–350 mg/L), and lactic (760–1080 mg/L) acid [40,167]. When the final product in the fermentation broth is acetic acid and butyric acid, the produced theoretical maximum hydrogen is 4 mol H_2/mol glucose, and 2 mol H_2/mol glucose respectively (equations (8) and (10)). The propionic acid and malic acid were reported to consume biohydrogen (equations (9) and (11)), and for ethanol, the produced biohydrogen is zero (equation (12)) [40,272].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \text{ (acetic acid pathway)} \quad (8)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \text{ (propionic acid pathway)} \quad (9)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \text{ (butyric acid pathway)} \quad (10)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow COOHCH_2CH_2OCOOH + CO_2 \text{ (malic acid pathway)} \quad (11)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2OH + CO_2 \text{ (ethanol pathway)} \quad (12)$$

These byproducts are commonly called dead-end products during fermentative biohydrogen production since they can't be further converted to biohydrogen spontaneously due to the thermodynamic limitation, however, coupling MEC with the dark fermentative process could overcome that barrier and allow further decomposition of those VFAs and alcohols for biohydrogen enhancement.

5.9. Lignocellulosic biomass pretreatment-linked inhibitors

During lignocellulosic agricultural residues pretreatment, some methods generate inhibitors as discussed in section 3. Those nano-sized products permeate the cytoplasmic membrane of hydrogen-producing bacteria to invade the internal structures and subsequently inhibit the synthesis of nucleic acid and protein [41,42]. The weak acids impede the transport of sugar within the cell, inhibit the regeneration of ATP and glycolytic enzymes which thus inhibit the growth of those bacteria responsible for hydrogen production [41,42]. The furfural and furan derivatives significantly inhibit carbon metabolism and the synthesis of the amino acid which harms the cell organelles. Therefore, the produced inhibitors from pretreated agriculture residues, inevitably decrease biohydrogen yields [41]. In 2020, Lin et al. reported that furfural, vanillin, 5-HMF, and syringaldehyde toxic byproducts significantly inhibited the biohydrogen production process from corn stover hydrolysate by employing *Thermoanaerobacterium thermosaccharolyticum W16* as pure inoculum [273]. The biohydrogen yield was reduced by 50.2%, 17.9%, and 54.3% in the presence of 5-HMF, furfural, and syringaldehyde respectively. Other investigators such as Siqueira and Reginatto also confirmed the negative effects of those inhibitors on biohydrogen production from the mineral medium with glucose [41,274]. When employing *E. aerogenes* and *E. coli* co-culture, Sharma et al. also reported a significant reduction of biohydrogen yield of 42.26%, 49.40%, 27.0%, and 37.2% after adding syringaldehyde, vanillin, furfural, and 5-HMF respectively [275]. The mixed of levulinic acid (2.1 g/L), formic acid (0.8 g/L), and 5-HMF (0.6 g/L) were also reported to decrease the biohydrogen yield by 89% and 83% when using *C. acetobutylicum* ATCC 824 and *C. beijerinckii* Br21 respectively [41,276].

6. Challenges of MEC -DF integration systems towards optimization and sustainable implementation at large-scale

Notwithstanding the advantages of MEC-DF as above mentioned, it is still facing numerous challenges that's need to be handled to ensure its sustainable industrial application. Firstly, the MEC-DF start-up process takes an average of weeks to months, which does limit industrial-scale applications. Therefore, a promising strategy for accelerating the MEC-DF start-up should be verified for the sustainability of this application [194]. Another critical challenge for the sustainable implementation of the MEC-DF integrated system at a large scale is the applied electrode materials, and cathodic catalysts [194]. The most employed electrodes are carbon-based materials and when the cathodic potential becomes too negative, the electrodes subsequently experience high overpotentials, large voltage loss, and electrode corrosion. Moreover, the chemical complexity of the applied medium in the MEC-DF boosts corrosion formation, and surface blockages over a longtime and thus aggravates the deterioration of electrode materials [277,278]. Therefore, the novel electrode with high catalytic activity, high conductivity, stability, cost-effectiveness, durability, and corrosion resistance should be developed for reliable application [194,279]. Platinum (Pt) is commonly used in MEC as catalysts to lower overpotentials to the desired level, and remove the thermodynamic barrier to some extends which leads to appreciable electrosynthesis efficiency. However, it is not an economic application that can be industrialized since it too expensive and not cost-effective, and it is employed for a limited time.

Alternatively, considerable efforts should be directed in investigating the feasibility of employing the biological cathode that uses only microbial cells as biocatalyst. The microbial biocathode that uses electroactive microorganisms holds numerous advantages over metal-based cathodes such as being cheap, regularly rejuvenated, and not susceptible to corrosion [278,280]. However, the development and maturation of the microbial biofilm is still a long and complicated business, therefore, simple and easy ways to enhance the biofilm formation for a long-time application in the MEC-DF system are highly required. Another challenge is that the catalytic activity of the biofilm is influenced by several factors that include the inoculum sources, feedstock compositions, electrode materials, and operation conditions, which don't support the industrial implementation of MEC-DF. The investigators need to take extra-care to guarantee the effectiveness and continuous biocatalytic activity at a large scale.

The membrane usually employed to separate anodic from cathodic chambers was reported so advantageous since it ensures high purity of biohydrogen by preventing eventual mixture of produced hydrogen with other anodic respiration by-products (CO_2, H_2S, etc.), and lessen hydrogen loss. However, it also causes several challenges towards the continuous application of bioelectrochemical systems at full scale. Over a long-time application, the complex chemical composition of the applied medium leads to the occurrence of the membrane fouling and subsequently decreases mass transfer rate, increases the internal resistance, and causes significant loss of voltage [135,188]. Therefore, the

use of the nitrifier-enriched activated sludge (NAS) as a source of inoculum to mitigate the bioreactor membrane fouling-associated issues as previously reported by Sepehri et al. [281] or to employ the membrane-less reactors would be technically more practical and promising approach towards sustainable implementation of the integrated MEC-DF system [194]. Nonetheless, the major limiting factor for practical biohydrogen production from agricultural residues in this system is the proliferation of methanogens which consume a part of produced biohydrogen and favor the generation of methane, thereby limit the purity of the produced biohydrogen [134,135]. For instance, Roland et all., performed a pilot-scale (1000 L) of continuous flow in MEC for biogas production from winery wastewater at sub-mesophilic temperature (15-22°c), and the detected gas was primarily (33 ± 22%), (51 ± 21%) and 21 ± 12% of H_2, CO_2 and CH_4 respectively. However, at the end of the experiment (day 97) with increased temperature, the CH_4 significantly increased to 86 ± 6% and no H_2 was detected at that time [282].

To control the proliferation of those undesired hydrogen-consuming bacteria (methanogens), several investigators have reported and suggested many strategies to inhibit their metabolic activities the existence which thus led to their extinction in the microbial biofilm. Those strategies include pH control, thermal, aeration (exposing the applied biocathodes to air), chemical (the incorporation of chemical compounds that act as methanogenic bacterial growth inhibitors such as 2-chloroethane sulfonate, 2-bromo-ethanesulfonate, and 8-aza-hypoxanthine), regular nitrogen sparging to decrease the hydrogen retention time, and microwave pretreatment under different operating conditions [134,135,138–140]. However, the most used, and cost-efficient was heat pretreatment since it is an easy and more feasible method to inhibit methanogens growth and activate the hydrogen-producing bacteria [40,283]. Once all those aforementioned challenges are addressed accordingly, the MEC-DF integrated system could be industrialized and provide sustainable solutions to solve the global energy shortage and environmental problems.

7. Conclusion and future perspectives

Biohydrogen energy is the most propitious alternative renewable energy source to fossil fuel-based energy. Its production from a renewable cheap feedstock such as lignocellulosic agricultural residues (straw biomass) could be a sustainable carbon neutral and most cost-effective approach. Dark fermentation which has been widely employed to produce biohydrogen from lignocellulosic agricultural residues has shown drawbacks owing to the recalcitrance of lignocellulose structure which hinders the microbial hydrolysis reactions and accumulation of acid-rich intermediate by-products that limit its practical feasibility. MECs use bio-electrochemical reactions to upgrade H_2 production in a DF reactor by the rapid decomposition of the agricultural straw biomass, volatile fatty acids (VFAs), and other non-degradable organic matter. Therefore, coupling MEC with the DF system (MEC-DF) can be a most promising strategy to optimize the conversion of the pretreated lignocellulosic agricultural residues and by-products into bio-hydrogen. In this system, dark fermentation primarily converts substrates into biohydrogen, CO_2, and VFAs which is followed by the electrohydrogenesis process in MEC for further biohydrogen conversion efficiency.

Moreover, our current review work proposes that the generated leftover residues resulted from the MEC-DF system after undergoing biodegradation and electrochemical decomposition during the biohydrogen production, instead of leaving them in the field open environment, they could be employed in the agricultural sector specifically to serve as natural biofertilizer to replace the chemical ones since they enrich the essential nutrient such P, N, K, etc, which are indispensable for plants growth [36,284]. This approach will significantly reduce or eliminate the huge cost always spent on expensive commercial fertilizer. Therefore, the development of a mature MEC-DF integrated system for sustainable H_2 production and a promising way for lignocellulosic agricultural residues management, and an emerging strategy for providing cheap biofertilizer needs to be further upgraded for high yield and production rates, and encourage its large-scale application. The pretreatment of the lignocellulosic agricultural residues is the indispensable process to overcome the recalcitrance issues for biohydrogen production, however, its high energy input and cost requirements are the major limitations for its practical application. Therefore, further studies should also focus much more on identifying microbial species that could directly biodegrade hemicellulose and cellulose.

It will remarkably simplify biomass pretreatment and make it more cost-effective. Once this strategy is successfully matured and applied on large scale, will undoubtedly satisfy the clean global energy demand, and simultaneously provide a sustainable way of agricultural residues management and durable cheap natural biofertilizer needed in the agriculture sector to improve the soil quality.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2021.111078.

Credit author statement

Fabrice Ndayisenga: Conceptualization, Investigation, Formal analysis, and Writing – original draft. Irfan Ali Phulpoto and Telesphore Habiyakare: Software, and Validation. Jianzhong Zheng, Dandan Zhou, Bobo Wang, and Hongxia Liang: Writing – review & editing. Zhisheng Yu: Conceptualization, Supervision, Funding acquisition, Project administration, Writing – review & editing. All authors read and approved the final manuscript.

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