Organic waste to biohydrogen

A critical review from technological development and environmental impact analysis perspective

Tian, Hailin; Li, Jie; Yan, Miao; Tong, Yen Wah; Wang, Chi Hwa; Wang, Xiaonan

Published in:
Applied Energy

Link to article, DOI:
[10.1016/j.apenergy.2019.113961](https://doi.org/10.1016/j.apenergy.2019.113961)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Tian, H., Li, J., Yan, M., Tong, Y. W., Wang, C. H., & Wang, X. (2019). Organic waste to biohydrogen: A critical review from technological development and environmental impact analysis perspective. *Applied Energy*, 256, [113961]. <https://doi.org/10.1016/j.apenergy.2019.113961>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Organic waste to biohydrogen: A critical review from technological development and environmental impact analysis perspective

Hailin Tian^a, Jie Li^b, Miao Yan^c, Yen Wah Tong^{a,b}, Chi-Hwa Wang^b, Xiaonan Wang^{b,*}

^aNUS Environmental Research Institute, National University of Singapore, 1 Create Way, 138602, Singapore

^bDepartment of Chemical and Biomolecular Engineering, National University of Singapore, 117585, Singapore

^cDepartment of Environmental Engineering, Technical University of Denmark, Bygningstorvet Bygning 115, 2800 Kgs. Lyngby, Denmark

*Corresponding Author: Xiaonan Wang, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore; Phone: (+65) 66016221; E-mail: chewxia@nus.edu.sg

Abstract

The increasing worldwide population and rapid urbanization have led to huge amount of fossil fuels consumption and waste generation. The awareness of living in a sustainable society is pushing people to target a low-carbon energy structure. Hydrogen, a carbon-free energy source, draws more and more attention. Particularly, biohydrogen from organic waste calls great interest by generating hydrogen and disposing waste simultaneously. Therefore, the three main technologies converting waste to biohydrogen: biological fermentation, thermochemical gasification and microbial electrolysis cell, were reviewed in this study from both technological and environmental perspective. The results showed that a variety of waste streams have been tested to produce hydrogen and different production efficiency were reported. The most favourable waste material for fermentation and microbial electrolysis cell were different types of wastewater, and agricultural lignocellulosic waste was also intensively studied in fermentation. Whereas wooden waste and municipal solid waste were the two wastes investigated the most in gasification. Optimization of the operational parameters was proved to improve the hydrogen production. However, researches focusing on scale-up of these technologies are still needed. On the other hand, life cycle assessment demonstrated that waste gasification had a better environmental profile compared to other technologies. However, the majority of the reviewed life cycle assessment studies failed to further explain the robustness due to the lack of sensitivity and uncertainty analysis, indicating high quality life cycle assessment studies are needed in the future.

Keywords

Biohydrogen production; Fermentation; Gasification; Microbial electrolysis cell; Life cycle assessment; Greenhouse gas emissions.

Contents

1	Introduction.....	4
2	Current technologies for biowaste to biohydrogen.....	8
2.1	Bibliographical statistics of the published papers	9
2.2	Biological fermentation	12
2.3	Thermochemical gasification	49
2.4	Microbial electrolysis cells.....	62
3	Environmental impacts analysis of biohydrogen from waste.....	76
3.1	Life cycle assessment	76
3.2	Bibliographical statistics of the selected LCA studies	88
3.3	Detailed research status progress.....	91
4	Comparison, challenges and future perspectives.....	97
5	Conclusions.....	104
	Acknowledgements.....	105
	References	105

1 Introduction

The world population is experiencing high growth rate, as well as rapid urbanization particularly in developing countries. To sustain the development of the society, the worldwide energy consumption has shown an increasing trend in the past years (Fig. 1) from less than 9,000 million tonnes of oil equivalent (Mtoe) in 1990 to above 14,000 Mtoe in 2018 with fossil fuels dominated in the energy structure [1], and it was predicted to reach at around 20,000 Mtoe in 2050 [2]. Consequently, huge amount of greenhouse gas (GHG) emissions has been released (Fig. 1), which resulted in environmental issues, such as global warming and the emergence of extreme weather. Therefore, different international, regional and national regulations and agreements have been proposed to reduce the GHG emissions. For example, the Paris Agreement has been signed by 195 members of the United Nations Framework Convention on Climate Change aiming to achieve a low GHG emissions and climate-resilient development mode. China, as the largest GHG emissions contributor in the world, promised to reduce 60-65% GHG emissions intensity (the unit emissions per dollar GDP) by 2030 compared to the level in 2005 [3]. According to the “2030 climate & energy framework” published by European Union (EU) Commission, 43% and 30% of GHG emissions reduction (compared to 2005) need to be achieved by 2030 for EU emissions trading system (ETS) sectors and non-ETS sectors, respectively. On the other hand, different human activities are producing considerable amount of waste, such as municipal solid waste, agricultural and animal waste, sewage sludge, etc., and the population explosion further contributes to the waste generation. United Nations (UN) reported that 2.0 billion tonnes of municipal solid waste (MSW) was generated in 2016 and the amount is expected to reach at 3.4 billion tonnes by 2050 [4], which makes the waste management a big challenge. Therefore, utilizing the

massive waste to produce energy towards a low GHG emissions society is on the international agenda that is important and urgent to solve [5].

Fig. 1. Worldwide total energy consumption and energy-related CO₂ emissions in each year: the historical data (year 1990-2018) were extracted from Enerdata (Global Energy Statistical Yearbook 2019); while the predicted data (year 2019-2050) were taken from U.S. Energy Information Administration (International Energy Outlook 2017)..

Over the past decades, different waste-to-energy technologies have been proposed and developed, such as incineration, gasification, anaerobic digestion, etc., depending on the different physic-chemical characterization of the waste [6]. The forms of the recovered energy vary from direct electricity and heat to different chemical energy including hydrogen, methane, ethanol, etc. [7]. Among them, hydrogen is considered as the cleanest energy carrier due to its zero end-use emissions with only water as the byproduct [8, 9], which results in an increasing research trend in these years. Moreover,

the energy content (low heating value) of hydrogen (120 MJ/kg) is also higher than most of the other energy sources, such as liquefied natural gas (54.4 MJ/kg), ethanol (29.6 MJ/kg) and methane (50.0 MJ/kg) [8, 10]. Furthermore, hydrogen also has a broader application in different areas compared to other forms. Currently, around 55% of the worldwide produced hydrogen is used for ammonia production, while 25% and 10% are used for petroleum refinery and methanol production, respectively [11]. Besides, hydrogen can also be used for direct combustion to generate electricity and heat, as well as transportation fuel. Moreover, the potential utilization for transportation is expected to increase significantly in the future due to the increased number of hydrogen fuel cell vehicles and the increased hydrogen retail stations that are being installed in countries such as Japan and China [8, 12]. However, in the current global hydrogen production market (> 50 million tons per year), more than 90% is generated from fossil fuels mainly through steam methane reforming and coal gasification, which results in huge GHG emissions [7, 13]. Water electrolysis technologies, including alkaline electrolyser, proton exchange membrane (PEM) electrolyser and solid oxide electrolyser, contribute to almost all the rest hydrogen production (< 10%), while hydrogen from other sources is negligible. Considering the fossil fuel is unrenewable and its price is more and more expensive, finding alternative cheap raw materials and technologies to produce hydrogen is inevitable in the future. Moreover, it was reported by the International Energy Agency that biohydrogen can contribute to significant reduction of GHG emissions because of its low-carbon footprint [12]. Therefore, hydrogen production from renewable sources shows its attractiveness [14].

As mentioned previously, considerable amount of waste is produced every year, and carbon-based renewable organic compound occupied a significant proportion, such as

food waste, agricultural residuals, sewage sludge, etc. How to utilize these organic wastes efficiently to produce biohydrogen attracts researchers' attention. Different technologies, such as fermentation, gasification and microbial electrolysis cell (MEC), have been developed to produce hydrogen from different wastes and/or wastewater in the past decades [15, 16]. To improve the hydrogen yield, optimization of the operational parameters, reactor configurations and efficient microorganisms were investigated. On the other hand, with the increasing environmental issues, the research focuses are not only on increasing the efficiency of the technology itself, but also on evaluating the environmental impacts of the proposed technology [17]. Life cycle assessment (LCA) is a commonly used scientific methodology to quantify the potential environmental impacts by taking all the input and output materials, energy and emissions into consideration [18]. The application of LCA on waste-to-hydrogen technologies have been reported in these years focusing on different impact categories [19, 20]. Several reviews can be found focusing on different aspects of hydrogen production technologies, but most of them focused on specific topics of each individual technology, such as inhibitors during dark fermentation [21], sludge fermentation [22], biomass hydrothermal gasification [23], MEC reactor configuration [24], cathode materials and catalysts [25], etc. Some old reviews about waste-to-hydrogen technologies were reported, such as dark fermentation of agricultural waste and lignocellulose [26], but they were published several years ago. It seems that the available reviews are either limited by a small scope or not updated with the latest research activities. Moreover, the LCA studies of these different technologies were never reviewed, compared and discussed. Thus, a comprehensive review focusing on the research publications in the latest ten years from both technological development and environmental impact analysis perspective cannot be avoided.

Therefore, focusing on the hydrogen generation technologies that use organic wastes as feedstocks, the main objectives of this review are to 1) present a holistic overview of the state-of-the-art of different waste-to-hydrogen technologies, including fermentation, gasification and microbial electrolysis cell; 2) summarise the environmental impact analysis of different waste-to-hydrogen technologies based on available LCA studies; 3) identify the bottleneck of current research and discuss the areas of additional research that could potentially improve the hydrogen production efficiency and environmental performance of different technologies.

2 Current technologies for biowaste to biohydrogen

Hydrogen plays an important role in different areas, such as in chemical industrial as the building block for other chemicals and in transportation as a fuel/energy source [27]. However, the majority of the worldwide hydrogen is currently produced from unrenewable sources, i.e. fossil fuels, while the contribution of biohydrogen is limited, particular from bio-residuals, such as different organic wastes and wastewater [17]. Thus, research on utilizing biowaste to produce biohydrogen has become a hot topic in recent years. As shown in Fig. 2, the current widely developed and discussed technologies that produce biohydrogen from waste materials include biological fermentation (dark fermentation and photo fermentation), gasification and MEC system [15, 28, 29]. The biological fermentation process relies on the activity of different microorganisms to decompose the complex waste polymers and produce hydrogen at the same time. The working conditions of these microorganisms are versatile that some of them are sensitive to light and prefer dark condition (dark fermentation), while some of them need light as energy source to proliferate (photo fermentation). The MEC system is modified from microbial full cell system, in which microorganisms also play a key role. The hydrogen

is produced in the cathode of the MEC, while the organic matters is oxidised in the anode to provide electrons for the cathode. Whereas the gasification is different from either fermentation or MEC because it is a thermochemical process that relies on high temperature and sometimes high pressure. The followed sections will focus on a detailed review of the technological development in the past ten years.

Fig. 2. An overview of the main biowaste to hydrogen technologies.

2.1 Bibliographical statistics of the published papers

In the past ten years, researches on the aforementioned technologies have been intensively conducted and the number of publications also showed an increasing trend (Fig. 3). With more than 800 articles published, gasification became the most studied technology, followed by biological fermentation; while the MEC was the least studied. A lot of factors can result in such a statistical distribution of the three technologies, such as different preferred substrates/feedstocks, different maturity of each technology, etc. Within the fermentation technology, the number of dark fermentation studies is almost three times higher than that of photo fermentation, which might be due to the simpler

reactor configuration of dark fermentation compared to the expensive and complex light source installation of photo fermentation [30]. Regarding the research activities from the geographical point of view, China performed very well and was always among the top two countries that performed most researches in all the three technologies. This might be explained by that China, as a new emerging and huge economy body, has exponentially increasing investment on research. Besides, India did a lot of researches on hydrogen production from waste through biological fermentation, which was followed by EU countries, such as Italy and France. In general, the Asian countries/regions (China, India, Turkey, South Korea, Taiwan, Malaysia, etc.) were more active in the fermentation researches compared to other countries and were involved in almost half of the research activities. Regarding the hydrogen generation through gasification, it is China and United States that did the most of the studies, while United Kingdom, Malaysia, Japan, Canada and Italy also performed many gasification researches. Moreover, the majority of the MEC studies all over the world were also performed in United States and China. However, it must be mentioned that even with such big amount of published researches, the full-scale application of these technologies on producing hydrogen from biowaste is still limited, especially for MEC technology which still stays at pilot-scale testing stage without any reports of full-scale commercialization.

Fig. 3. The statistics of papers about biohydrogen production from biowaste through “biological fermentation”, “gasification” and “microbial electrolysis cells” that were published in the past ten years (2009-2018) based on the “Scopus database”: a) the number of papers published in each year; and the number of publications from the top ten countries who contributed the most of the studies of b) dark fermentation, c) photo fermentation, d) microbial electrolysis cells and d) gasification.

2.2 Biological fermentation

A variety of microorganisms are capable to decompose organic waste and wastewater to produce hydrogen with organic acids/alcohols as the main byproducts under anaerobic condition, so-called fermentation. According to the characteristics (necessity of light) of the microorganisms, the biological fermentation is separated into two different types: dark fermentation and photo fermentation. To improve the hydrogen production efficiency, integrating the two types of microorganisms together has also been reported. The concept of different types of fermentation were shown in Fig. 4.

Fig. 4. A schematic diagram of different types of biological fermentation: a) dark fermentation, b) photo fermentation, c) combined dark and photo fermentation, and d) sequential dark and photo fermentation. The black dots and short wave and straight lines were used to stand for the functional microbiota for dark fermentation; while the purple and green wave and straight lines were used to stand for the functional microbiota for photo fermentation.

2.2.1 Dark fermentation

Dark fermentation, which depends on microorganisms to produce hydrogen under anaerobic and dark condition, has been developed as a well-known hydrogen producing technology in the past decades [31]. As shown in Eq. (1), the hydrogen formation is a result of the reduction of protons by the electrons generated during other carbon source degradation. In general, there are two different hydrogenases that participate in this hydrogen formation process, i.e. [FeFe]-hydrogenase and [NiFe]-hydrogenase [32]. Theoretically, 12 mol hydrogen should be produced from one mol glucose (Eq. (2)).

However, due to the other byproducts generation, such as acetic acid (Eq. (3)), butyric acid (Eq. (4)), propionic acid (Eq. (5)), etc., the hydrogen production efficiency is always lower than the theoretical value. Actually, throughout the available literatures, 3.47 mol H₂/ mol glucose was found to be the maximum hydrogen yield in dark fermentation process [33]. Based on the different byproducts, the hydrogen production through dark fermentation are classified as the following four different types [34]: propionate-type fermentation, butyrate-type fermentation, ethanol-type fermentation and mixed-type fermentation, while the hydrogen yield varies among the different hydrogen production types.

Dark fermentation of the pure carbohydrate substrates, such as glucose and starch, has been proved to be an efficient hydrogen producing method, but the pure chemicals are too expensive to use. Thus the organic matters from the waste materials are considered as a cheap and easy-accessible source for hydrogen production. Intensive studies have been performed in the past years to optimize the hydrogen production from waste materials based on dark fermentation. Different factors that can influence the hydrogen yield in dark fermentation process, including the variety of the feedstocks, different

reactor types, operational parameters (pH, temperature, hydraulic retention time, etc.) and also the microbial community, were investigated.

2.2.1.1 Different waste feedstocks

A variety of waste materials have been used to produce hydrogen. As shown in Fig. 5, the most widely studied waste including different kinds of wastewater (e.g. cheese whey effluent, distillery wastewater, palm oil mill effluent, etc.) and agricultural waste (e.g. animal manure, rice/corn/wheat straw, etc.), followed by food waste, sewage sludge and MSW. The chemical compositions of the waste determines the hydrogen yield (in terms of per unit volatile solid (VS) or chemical oxygen demand (COD)). Alibardi and Cossu [35] demonstrated that the hydrogen production has a linear correlation with carbohydrate proportion in the waste composition, while proteins and lipids have an insignificant contribution. Moreover, Xia et al. [36] investigated the co-fermentation of monosaccharide and amino acids, and found that the final hydrogen production was mainly from monosaccharide other than amino acids, and the consumption of monosaccharide was much faster than amino acids. Thus it can also be seen from Table 1 that waste such as palm oil mill effluent and sewage sludge usually had a lower hydrogen production compared to other wastes due to the high content of either lipid or protein.

Fig. 5. The number of publications about dark fermentation of different waste materials in the past ten years (2009-2018). The “Agricultural waste” takes straw, manure, cornstalk, sugarcane and other agricultural lignocellulosic waste together into consideration. The data source comes from “Scopus database”.

Besides the different waste materials themselves, research focus has also been placed on the application of pretreatment to improve the hydrogen production efficiency. Therefore, different pretreatment methods, such as mechanical (milling and grinding), physical (high temperature, microwave and ultrasonication), chemical (acids, bases and oxidation), radiation, hydrothermal and enzymatic pretreatment, were investigated by different researchers [9, 37-42]. Dairy manure was pretreated with three different methods: 1) 0.2% (w/w) HCl solution, 2) 0.2% (w/w) NaOH solution, and 3) infrared oven for 2 hours; while the substrate solid loading was 10% (w/w) in method 1) and 2), then both mixtures were boiled for 30 min and neutralized pH to 7.0. However, only the acid treatment had a significant hydrogen yield improvement of 36.1% compared to the untreated manure, while base and infrared oven only improved 6.8% and 4.5% [42]. Leañó and Babel [41] studied the influence of enzyme (Optimase BG[®]) and surfactant

(Tween 80[®]) on hydrogen production from palm oil mill effluent. An improvement on the hydrogen yield of 66% and 335% was observed for enzymatic and surfactant pretreatment, respectively. Moreover, the lignocellulosic materials from agricultural waste, such as cornstalk, rice/wheat/corn straw, sugarcane bagasse, etc., have attracted attentions in many different areas, including bioethanol production and biorefinery concept, as well as in biohydrogen production. However, due to the specific chemical structure of lignocellulose, it is difficult for the hydrogen-producing bacteria to break down the lignocellulose polymers into monomers, i.e. sugars [43]. The pretreatment investigation on lignocellulosic materials were also intensive [37, 44-47]. For example, the hydrogen yield of lime pre-treated cornstalk (155 mL H₂/ g VS) was found to be 35% higher than the untreated one (115 mL H₂/g VS) [46]. Moreover, Gonzales and Kim [47] studied the pretreatment of rice husk by sequential dilute sulfuric acid treatment and a commercial enzyme treatment. After the pretreatment, the highest hydrogen yield was found to be 473 mL H₂/g rice husk, while 321 mL H₂/g rice husk were observed with only dilute acid pretreatment.

Researchers also found that the fermentation of single waste type usually cannot achieve a high hydrogen production. Nevertheless, co-fermentation of different waste types might result in synergistic effect followed by a high yield and efficiency [48]. For example, the hydrogen production from solo sewage sludge fermentation was low (11.2 mL/g VS), while the yield increased to 20.8, 32.0, and 51.7 mL/g VS when co-fermented with fallen poplar leaves, flower waste, and sheared ryegrass, respectively [49]. Co-digestion of food waste and sewage sludge (92.5 mL H₂/g VS) resulted a 90% improvement of the hydrogen production yield compared to solo food waste fermentation

(48.7 mL H₂/g VS) [50]. Moreover, the authors also found that the addition of crude glycerol could further increase the hydrogen yield up to 179.3 mL H₂/g VS.

Table 1. Some selected studies of waste disposal and hydrogen generation through dark fermentation.

Waste type	Detailed waste information	Microorganism	Pretreatment	Reactor type	Temperature (°C)	pH	H ₂ yield	Ref.
Wastewater	distillery wastewater	Mixed culture	Neutralization to pH 6.7, centrifugation at 5000 rpm and sterilization	Batch	37	maintained above 5.0	1.6±0.3 L/L wastewater	[51]
	palm oil mill effluent	Mixed culture	Ultrasonication at 195 J/mL	Batch	44	initial pH 7	1.19 mmol/g COD	[40]
	palm oil mill effluent	Mixed culture	Two different ways: Enzyme Optimase BG [®] and surfactant Tween 80 [®]	Batch	44	initial pH 7	Tween 80 [®] : 4.91 mmol/g COD Optimase BG [®] : 1.88 mmol/g COD	[41]
	Sago-processing wastewater	Mixed culture	-	Batch	30	initial pH 7	456 mL/g starch	[52]

	cassava wastewater	Mixed culture	-	UASB	37	Controlled	39.8 mL/g COD	[53]
				Continuous		at 5.5		
Agricultural waste	Swine manure	Mixed culture	Microwaved with 1% H ₂ SO ₄ for 15 min	Batch	35 ± 1	Initial pH 6.0	71.8±5.19 mL/g VS	[54]
	Dairy manures	Mixed culture	0.2% HCl treatment at solid loading of 10% and boiled for 30 min, then adjust pH to 7.0	Batch	36 ± 1	Controlled at 5.0	31.5 mL/g VS	[42]
	Sugarcane bagasse	<i>Enterobacter aerogenes</i>	2% sulphuric acid (v/v) in solid and liquid mass ratio 1:15, then autoclaved	Batch	30	Initial pH 6.8	1000 mL/L hydrolysate	[44]
	Rice straw	<i>Clostridium pasteurianum</i>	Cut and grinded in 2 mm size, 1.0% alkali and	Batch	37 ± 2	Initial pH 7.5	2580 mL/L hydrolysate (47.6 mL/g released sugar)	[55]

			nanomaterial pretreated, then hydrolysed with cellulase					
	Wheat straw	Mixed culture	Hydrothermal pretreatment	Batch & CSTR continuous	70	-	Batch: 14.2 mmol/g sugar CSTR: 7.9 mmol/g sugar	[45]
Food waste	Food waste hydrolysate	Mixed culture	Raw waste pretreated by glucoamylase and protease	Batch	37	Controlled at 4.0-4.6	219.9 mL/g VS	[56]
	Food waste from fast food restaurant	<i>Escherichia</i> <i>cloacae</i>	Ground and mixed thoroughly in a blender	Batch	37 ± 1	Controlled at 5.0-6.0	155.2 mL/g VS	[57]
	Food waste from school cafeteria	No external inoculum	Ground into less than 5 mm	Batch	50	Initial pH at 8.0, then controlled at 6.0	137.2 mL/g VS	[58]

Sewage sludge	Sewage sludge	Mixed culture	Boiled at 100 °C for 15 min	Batch	37	Initial pH at 7.0	11.2 mL/g VS	[49]
	Primary sewage sludge	Mixed culture	Pasteurisation (70 °C for 1 h) and enzyme cellulase	CSTR continuous	35	Controlled at 5.5	21.9-32.7 mL/g VS	[59]
Municipal solid waste	OFMSW from a MBT plant	Mixed culture	-	CSTR continuous	55	Feeding pH at 5.5	24.3 mL/g VS	[60]
	OFMSW contains fermentescible waste, paper and cardboard	No external inoculum	Ground to a particle size below 16 mm	Batch	35	Controlled at 5.5	57.3 mL/g VS	[61]
Co- fermentation	Sewage Sludge co- digested with poplar leaves (SP), flower waste (SF), and ryegrass (SR), respectively	Mixed culture	Sludge: boiled at 100 °C for 15 min Other waste: washed with deionized water and then dried at 60 °C	Batch	37	Initial pH at 7.0	SP: 20.8 mL/g VS SF: 32.0 mL/g VS SR: 51.7 mL/g VS	[49]

Fruit/vegetable waste and swine manure	Mixed culture	Shredded in a blender	Semi-continuous	55 ± 1	Not adjusted	The highest yield: 126 mL/g VS	[62]
Food waste and crude glycerol	Mixed culture	Food waste was shredded in a kitchen mill	Batch	35 ± 1	No adjusted	The highest yield: 180 mL/g VS	[63]
Food waste, sewage sludge and crude glycerol	Mixed culture	Sewage sludge was pretreated at 100 °C for 30 min	Batch	35 ± 1	Initial pH at 5.5	The highest yield: 179.3 mL/g VS	[50]

*Some abbreviations: MBT: Mechanical-biological-treatment; OFMSW: Organic fractions of municipal solid waste; CSTR: Continuously stirred tank reactor; UASB: Upflow anaerobic sludge blanket reactor; VS: Volatile solid; COD: Chemical oxygen demand.

2.2.1.2 Different operational parameters

Fermentation process relies on different microorganisms, and temperature is a key factor that affects the microbial growth, consequently influences the hydrogen yield and efficiency. The bacteria have a broad living temperature range from -20 °C to 122 °C [64]. However, mesophilic (25-45 °C) and thermophilic (45-65 °C) conditions are the most widely investigated and reported temperature ranges. Specifically, the optimal fermentation temperatures for mesophilic and thermophilic conditions can be further narrowed down to 35-40 °C and 50-60 °C, respectively [65]. It is reported by Xiao et al. [57] that the hydrogen yield of food waste was much higher at 37 °C compared to 21.5 °C. Kim et al. [58] also studied the hydrogen production from food waste without external inoculum under 35, 40, 45, 50, 55 and 60 °C. The results indicated that the hydrogen yield increased along with the increase of the temperature up to 50 °C, but decreased with further temperature increase. However, the opposite phenomenon was found that the hydrogen production of raw cheese whey wastewater at mesophilic (36±1 °C) was higher than that at thermophilic (55±1 °C) condition [66]. Therefore, in general, the higher of the temperature it uses in dark fermentation, the higher hydrogen yield should be observed within a certain temperature range. However, opposite cases also exist depending on the characteristics of the used microorganisms, which might result in a lower hydrogen production at higher temperature but with a high volatile fatty acids (VFA) production.

The pH level of dark fermentation is another important parameter. It influences not only the microorganism activity and metabolic pathway, but also the cell morphology and intracellular pH. Important attention should be paid to distinguish between the initial pH level when the dark fermentation starts and the operational pH throughout the whole fermentation process. Some researchers investigated the pH impact by adjusting the pH

level at the beginning of fermentation without pH control after the initiation of the fermentation process; while other researchers studied the pH influence by controlling a constant pH level from the beginning until the end of the fermentation. The main difference is that a decrease of the pH level was usually observed due to the VFA production if the pH was not controlled. Generally speaking, the optimal pH range for dark fermentation is 5-7 depending on the dominant hydrogen-producing microorganism, as well as the feedstocks [67]. Guo et al. [26] concluded that the optimal pH level for food waste and crop straw were 5.0-6.0 and 6.0-7.0, respectively. A wide constant operational pH range from 4.0 to 12.0 with a pH gap of 1.0 unit was applied to dairy manure fermentation, the highest hydrogen yield was observed at pH 5.0 [42]. It also indicated that the hydrogen production almost ceased when the pH was at 4.0 or higher than 9.0. Moreover, Azbar et al. [66] studied the influence of different initial pH levels on hydrogen production from cheese whey wastewater, including pH at 4.5, 5.5, 6.5 and 7.5, in which the highest cumulative hydrogen production was achieved at pH 6.5 under mesophilic condition and at pH 5.5 under thermophilic condition, respectively.

Hydrogen partial pressure plays a crucial role in hydrogen production efficiency and also the gas-liquid compositions, this is mainly because the oxidization and reduction of ferredoxin by hydrogenase is a reversible process. Thus keeping a low hydrogen partial pressure by removing the produced hydrogen in the reactor is of great importance. Methods such as stirring, sparging and vacuuming, have been investigated. For example, increasing the stirring rate from 20 rpm to 100 rpm improved the hydrogen production of spent grain [68]. A reduction of the hydrogen partial pressure through vacuum was found to promote the diversity of hydrogen-producing bacteria, and consequently resulted in an enhancement of hydrogen production [69]. Moreover, sewage sludge was used to produce

hydrogen in continuous condition with two methods increasing the removal of the produced hydrogen: sparging the reactor and flushing the reactor headspace with nitrogen at a rate of 60 mL/(L·min) [59]. The results showed that the hydrogen yield increased by 121% and 56% with sparging and flushing method, respectively, compared to the untreated reactor. However, even though different hydrogen removal methods have been proposed and an increase of hydrogen production has been observed, investigation on efficient and cheap methods should be further developed, especially in continuous hydrogen production mode.

In continuous biohydrogen production process, the hydraulic retention time (HRT), which determines the fermentative duration of the substrate, is another important operational parameter that influence the feedstock utilization efficiency and the overall stability of the reactor. The HRT depends highly on the substrate characterization, especially the biodegradability, i.e. the easier the substrate to degrade, the lower the HRT is. However, the HRT cannot be too low, which should be at least longer than the doubling time of the bacteria to allow the proliferation of the bacteria. Massanet-Nicolau et al. [59] investigated sewage sludge fermentation in a 5 L CSTR reactor under four different HRTs, i.e. 18, 24, 36 and 48 h. The authors concluded that 24 h was the optimal HRT for sewage sludge degradation with a yield of 21.9 mL H₂/g VS. In the mixed culture dark fermentation system, a decrease of the HRT can limit the microbial diversity towards a more specific hydrogen production community by eliminating the methanogens and other bacteria that need a longer doubling time to grow. By decreasing the HRT from 12 to 6 hours for the degradation of steam exploded switchgrass liquor and from 8 hours to 4 hours for the degradation of cassava processing wastewater, the hydrogen production yield for the both cases increased significantly [70, 71]. Moreover, compared to other

biological energy recovery technologies, such as bioethanol fermentation and anaerobic methane production (counted by days), dark fermentation usually has a shorter HRT (usually counted by hours), which also highlights the benefit of hydrogen production from waste materials through dark fermentation.

2.2.1.3 Hydrogen-producing microbiology

Fermentation is a biological process and different microorganisms are involved in this process. Throughout the available studies, varieties of pure hydrogen-producing strains and mixed culture have been identified. According to different living temperatures, the hydrogen-producing microorganisms can be classified as psychrophiles (0-25 °C), mesophiles (25-45 °C) and thermophiles (45-65 °C), among which mesophiles and thermophiles are the most studied ones; while according to the tolerance of hydrogen, they can be categorised into strict anaerobes and facultative anaerobes.

A lot of pure strains that belong to different genus were isolated and identified in the past years. The common mesophilic hydrogen-producing cultures are *Clostridium* spp. and *Enterobacter* spp., such as *Clostridium butyricum*, *Clostridium beijerinckii*, *Enterobacter asburiae* and *Enterobacter aerogenes*; while *Thermoanaerobium* spp. is the mostly reported thermophilic bacteria, such as *Thermoanaerobacterium thermosaccharolyticum* [34]. Meanwhile, other genus were also reported in literatures, such as *Ethanoligenens*, *Bacillus*, *Escherichia*, etc. Xiao et al. [57] investigated nine different species: two from genus *Escherichia*, two from genus *Enterobacter* and five from genus *Clostridium*, on the hydrogen production efficiency of food waste. The results showed different performance on the final hydrogen yield, and *Escherichia cloacae* and *Enterobacter aerogenes* had the highest hydrogen production yield among all the tested strains. *Clostridium butyricum* was immobilized in a polyethylene glycol gel for hydrogen

production from palm oil mill effluent, and resulted in a high hydrogen yield and production rate [72]. Moreover, apart from using one single pure strain, co-culture of different pure strains were also reported. It was reported that when co-culture of *Enterobacter aerogenes* and *Clostridium butyricum* was used as inoculum, the hydrogen yield of biodiesel industry waste was higher than either of single strain [73]. The same phenomenon was also found by Phowan et al. [74] when co-culture of *Enterobacter aerogenes* and *Clostridium butyricum* was used to degrade cassava pulp hydrolysate to produce hydrogen.

However, the pure strain cultivation environment is normally strict, which needs specific medium and sterilized condition. Thus mixed culture with a much more diverse microbial community has been investigated and applied in these years, particular to the complex waste that needs upstream degradation, such as hydrolysis. The mixed culture can be obtained from different sources, such as anaerobic digester, animal compost, sediment, leachate, etc. [49, 66, 75-77]. However, the hydrogen production efficiency of the inocula from different sources also performed differently. For example, the mixed culture taken from activated sludge produced 2.2 times higher hydrogen than the one taken from cow dung compost when rice straw was used as substrate [78]. Due to the complex microbial community, other microorganism groups also exist, including the beneficial bacteria that can help hydrolyse the polymers, but also the unwanted hydrogen consumers such as methanogenic archaea and homoacetogenic bacteria, as well as other microbes that compete for the substrates and nutrients with the hydrogen-producing bacteria. Therefore, different pretreatment methods are usually needed for the mixed culture before using it to produce hydrogen, which is done in order to enrich hydrogen-producing bacteria but deactivate/eliminate/exclude the hydrogen consumers. The most

widely used pretreatment methods include heating, freezing and thawing, adding chemical inhibitors, microwave irradiation, ultrasonication, etc. [39].

2.2.2 Photo fermentation

Photo fermentation is another biological process that produces hydrogen by photosynthetic bacteria, mainly by purple non-sulfur bacteria (PNSB), in the presence of light and carbon source and the absence of oxygen and nitrogen [79]. The light source can come from either solar or different artificial sources; while the carbon source can be either simple sugar or different VFAs. As shown in Eq. (6-8), one mol glucose could theoretically produce 12 mol hydrogen; while other VFAs can produce different amount of hydrogen depending on its chemical characteristics. However, compared to dark fermentation, the degradation rate on different VFAs by photosynthetic bacteria is relatively slower. Moreover, it seems that PNSB prefer VFAs as substrate other than sugars, evidenced by its faster hydrogen generation rates with VFAs compared to pure sugars [80]. Therefore, integration of dark and photo fermentation together has been suggested and developed in recent years and a lot of researches have been performed.

Unlike dark fermentation that mainly relies on hydrogenase to drive the hydrogen production, photo fermentation produces hydrogen through nitrogenase. Actually, as

shown in Eq. (9), when one mol nitrogen is fixed through nitrogenase to ammonia, one mol hydrogen can be produced. Whereas hydrogen can be produced more efficiently in the absence of nitrogen, as shown in Eq. (10). Therefore, nitrogen source and C/N ratio in the substrate play an important role in hydrogen production through photo fermentation. Moreover, due to the necessity of light during photo fermentation, light efficiency is an important indicator to evaluate the system energy conversion rate. Therefore, not only light intensity, but also different wavelength, are crucial in this process, which makes the photo fermentation reactor design and operation much more complex compared to dark fermentation.

2.2.2.1 Different waste feedstocks

Despite the complexity of photo fermentation, researches are still available using photo fermentation to dispose different types of waste due to its high hydrogen conversion efficiency, as well as the high COD removal rate of waste/wastewater. As shown in Fig. 6, the most used waste stream in photo fermentation was different types of wastewater, such as brewery wastewater, dairy wastewater, olive mill wastewater, etc.; while agricultural waste after hydrolysis and dark fermentation effluent were also studied intensively.

Fig. 6. The number of publications about photo fermentation of different waste materials in the past ten years (2009-2018). The “Agricultural waste” takes straw, manure, cornstalk, sugarcane and other agricultural lignocellulosic waste together into consideration. The data source comes from “Scopus database”.

2.2.2.2 Different operational parameters

The favourable temperature range and pH for photo fermentation, as shown in Table.2, is between 28-32 °C and around neutral pH environment [81], while some specific microorganism strains can be outside the range working efficiently up to 35 °C. Nevertheless, up to date, none thermophilic studies of hydrogen production through photo fermentation can be found. Lu et al. [82] used rotten apples as feedstock to produce hydrogen at different temperatures (25, 30, 35, and 40 °C) and pH (4, 5, 6, 7, 8, 9, and 10). The experimental results were integrated using response surface methodology and the regression results predicted that the highest hydrogen yield could be obtained at 30.5 °C and pH of 7.1. The similar optimal pH level, i.e. 7.0, was also observed by Jiang et al. [83] when corn stalk pith was used as substrate to produce hydrogen at different pH levels, including 4, 5, 6, 7, 8, 9, and 10.

On the one hand, the efficient hydrogen production from PNSB is on the condition of the absence of nitrogen; on the other hand, nitrogen is one of the essential nutrients for the growth of microorganism. Thus the C/N ratio is of great importance in determining the hydrogen production. Androga et al. [84] investigated hydrogen productivity of *Rhodobacter capsulatus* YO3 at different C/N ratios and found C/N of 25 was the optimal choice. The authors also concluded that a low C/N ratio results in low biomass concentration and consequently low hydrogen yield, while a high C/N ratio can result a

high biomass concentration but decreased hydrogen productivity. However, not only the C/N ratio, but also the absolute ammonia concentration is crucial in photo fermentation. Inhibition on nitrogenase was observed with ammonia above 20 mM in the solution [85]. Therefore, adjusting an appropriate C/N ratio and controlling the ammonia concentration should be carefully considered during photo fermentation process.

In order to achieve an optimal balance between the production rate, substrate conversion efficiency and the invested light energy in photo fermentation process, an appropriate HRT is needed for continuous operational mode. The optimal HRT of photo fermentation is usually longer than dark fermentation due to the slower metabolic activity of PNSB compared to dark fermentation bacteria, and has a big range from one day up to five days [86]. When enzyme treated corncob was photo fermented at HRT of 12, 24, 36, 48, 60, and 72 h using mixed culture, the highest hydrogen yield and production rate was found to be at the HRT of 24 and 36 h, respectively [87]. However, in another study of *Rhodobacter sphaeroides* mediated photo fermentation treating the dark fermentation effluent of ground wheat starch, HRT of 24, 48, 72, 96 and 120 h were investigated, and it turned out that HRT of 72 h resulted in the highest hydrogen production rate and yield [88].

Different from dark fermentation, light is essential in photo fermentation that provides energy for the bacteria growth. Thus the studies of light application in photo fermentation, including the different intensities, sources and even wavelengths, were intensively performed in order to achieve a high light conversion efficiency, which is calculated as shown in Eq. (11).

$$\eta (\%) = (33.61 \times \rho_{H_2} \times V_{H_2}) / (I \times A \times t) \times 100 \quad \text{Eq. (11)}$$

Where η is the light conversion efficiency, ρ_{H_2} and V_{H_2} stand for the density and the volume of the produced hydrogen, respectively; while I is the light intensity, A is the irradiated area and t is the hydrogen production time.

As shown in Table 2, different light sources were reported in literatures in photo fermentation of different waste streams, including solar and artificial lights [85, 88, 89]. One of the distinct disadvantages of using solar is its instability, not only the unavailability during the night time, but also the changes along with the weather and season. Moreover, photo fermentation inhibition of sunlight at noon was reported [90], and it was reported that the light utilization efficiency of sunlight is usually lower than the optimized artificial illumination system. However, the significant advantage of sunlight is its reduction of the total investment of photo fermentation system. Other light sources, including light-emitting diode (LED), mercury–tungsten lamp, halogen lamp, were also used in these years. Nevertheless, tungsten lamp has a wide wavelength but a short lifetime, while LED has a long lifetime but a high price. With respect to light intensity, it seems that the optimal light intensity is influenced by several factors, such as the characteristics of the feedstock, the functional strains, etc. Different light intensities, including 500, 1000, 2000, 3000, 4000 and 5000 lux, were used for photo fermentation of rotten apples, and 3000 lux was found to be the best one achieving the highest hydrogen production [82]. However, in another study of dairy wastewater, four different light intensity of 4000, 5000, 9000 and 13000 lux were generated using mercury–tungsten lamp, in which the highest hydrogen yield was observed at 9000 lux [85]. It was reported that not only the light intensity but also the wavelength play an important role in photo fermentation process [91]. Moreover, the authors concluded that wavelength between 600-780nm was beneficial of hydrogen generation by *Rhodobacter sphaeroides*. In

another study of *Rhodopseudomonas palustris* CQK 01 treating glucose-based synthetic wastewater, three different wavelengths (470, 590 and 630 nm) and six light intensities (3000, 4500, 5000, 5500, 6000 and 8000 lux) were employed, and the highest hydrogen yield was found at wavelength of 590 nm and intensity of 5000 lux [92]. However, even at the optimal condition, the light conversion efficiency is still low, which is identified to be the bottleneck for the scaling up of photo fermentation to produce hydrogen. Four different pure PNSB strains, including *R. capsulatus* DSM 1710, *R. capsulatus* YO3, *R. sphaeroides* O.U.001 and *Rp. palustris* DSM 127, were individually used to produce hydrogen from sugar beet molasses with continuous illumination from tungsten lamp at 114 W/m^2 [93]. For all the strains with three different substrate concentrations, the highest light conversion efficiency was observed at 0.47% and the lowest one was 0.09%, which indicated a huge energy waste of the light. In another study of brewery wastewater treatment with *Rhodobacter sphaeroides* [94], a slight higher conversion efficiency of 1.7% was observed. However, in generally, the average light efficiency of the normal traditional photo reactor was reported to be 1-5%, and the highest conversion rate was limited within 10% [95, 96]. Therefore, different photo reactor configurations to optimize the light conversion rate were proposed [97], such as immobilized cell reactor, vertical column reactor, plate reactor, baffled stacking reactor, etc. A light conversion efficiency as high as 56% was reported in a biofilm reactor illuminating with LED at 590 nm and intensity of 5000 lux [92]. Ideally, the commercialization of photo fermentation will be further applied if the light conversion rate can reach close to 100%.

Table 2. Some selected studies of hydrogen production from photo fermentation.

Waste type	Microorganism	Pretreatment	Reactor type	Light Info	Temperature (°C)	pH	H ₂ yield	Ref
Maize straw	<i>Rhodobacter</i> <i>sphaeroides</i> HY01 and WH04	5% HCl at 118 °C for 30 min	Batch	4000 ± 200 lux	30	7.1-7.8	3.56 and 4.62 mol/mol reducing sugar for HY01 and WH04, respectively	[98]
Corn stalk pith	Mixed culture	Enzyme cellulase	Batch	2000 lux by filament lamps	30	Initial pH at 7	2.6 mol/mol sugar consumed	[83]
Brewery wastewater	<i>Rhodobacter</i> <i>sphaeroides</i>	Sterilized at 120 °C for 20 min	Batch	9000 lux by mercury– tungsten lamp	28 ± 2	Initial pH at 7.0-7.2	0.22 L/L waste	[94]

Dairy wastewater	<i>Rhodobacter</i>	Sterilized at	Batch	9000 lux by	28 ± 2	Initial	8.6 L/L waste	[85]
	<i>sphaeroides</i>	120 °C for 20 min		mercury–tungsten lamp		pH at 7.0-7.2		
Dark fermentation effluent of ground wheat starch	<i>Rhodobacter sphaeroides</i>	Supplement with several nutrients	Continuous	halogen lamps at 5000 lux	30	7.3	185 mL/g VFA	[88]
Dark fermentation effluent of sugarcane bagasse	<i>Rhodopseudomonas</i> BHU 01	Supplemented with the growth medium	Batch	8.5 W/m ² by tungsten lamp	34	6.8	755 mL/L waste	[44]
Sugar beet molasses	<i>R. capsulatus</i> DSM 1710, <i>R. capsulatus</i> YO3, <i>R. sphaeroides</i>	Buffer addition, pH adjustment, and sterilization	Batch	114 W/m ² by tungsten lamp	30	Initial pH at 7.4-7.5	<i>R. capsulatus</i> DSM 1710: 12.7 mol/mol sucrose <i>R. capsulatus</i> YO3: 10.6 mol/mol sucrose	[93]

	O.U.001 and <i>Rp.</i> <i>palustris</i> DSM 127						<i>R. sphaeroides</i> O.U.001: 9.4 mol/mol sucrose <i>Rp. palustris</i> DSM 127: 19.0 mol/mol sucrose	
Rotten apple	Mixed culture	Crushed and screened with 40-mesh sieve	Batch	3030 lux	30.5	7.1	112 mL/g TS	[82]
Sugar industry wastes: beet molasses and black strap	<i>Rhodobacter</i> <i>capsulatus</i> JP91	-	Batch	200 W/m ² by tungsten lamp	30	Initial pH at 7.0	beet molasses: 10.5 mol/mol sucrose black strap: 8.0 mol/mol sucrose	[99]
Dark fermentation effluent of corn stover	Mixed culture	Adjust pH to 7.0 and C/N to 10	Continuous	3000 lux by solar and	30	Initial pH at 7.0	4.7 m ³ /m ³ /d	[89]

				LED				
				bundles				
Olive mill	<i>Rhodobacter</i>	Mixed with	Batch	150 W	-	Initial	31.5 L/L waste	[100]
wastewater	<i>sphaeroides</i>	activate clay at		tungsten		pH at		
	O.U.001	pH 2, then get		lamp		6.7		
		the liquid part						

*Some abbreviations: VFA: volatile fatty acid; TS: total solid; LED: light-emitting diode.

2.2.2.3 Microorganisms in photo fermentation

In most of the studies, pure strains were chosen as functional bacteria for photo fermentation, while mixed consortia have also been used in different studies. It is generally accepted that anoxygenic photosynthetic microorganisms cover four main different phyla: purple sulfur bacteria (e.g. *Chromatium*), green sulfur bacteria (e.g. *Chlorobium*), purple non-sulfur bacteria (e.g. *Rhodobacter*) and green non-sulfur bacteria (e.g. *Chloroflexus*) [101]. Among them, purple non-sulfur bacteria (PNSB) are the most widely studied photosynthetic hydrogen-producing bacteria. The commonly used strains that belong to PNSB are as follows: *Rhodobacter* spp., *Rhodopseudomonas* spp., *Rhodobactersphaetoide* spp. and *Rhodobactersphaetoide* spp. [95]. However, researchers have also tried to isolate more and more pure and specific functional strains in these years. For example, several strains belong to species *Rhodopseudomonas capsulatus*, *Rhodopseudomonas palustris*, *Rhodopseudomonas sphaeroides* and *Rhodopseudomonas rubrum* were isolated recently from the trophic lake Averno [102]. Moreover, *Rhodobacter* sp. KUPB1 was also isolated as a halotolerant bacteria which can produce hydrogen with NaCl concentration up to 3% [103]. *Rhodopseudomonas* sp. nov. strain A7 and *Rhodobacter sphaeroides* CNT 2A, which was isolated from sludge and pond sediment, respectively, can directly utilize simple sugar, such as glucose and sucrose [104, 105]. It must be mentioned that different pure strains perform differently with respect to hydrogen yield from the same substrate. *Rhodobacter capsulatus* wild type, *R. capsulatus hup⁻* mutant, and *Rhodopseudomonas palustris* were used for sugar beet molasses fermentation and the hydrogen yield was in a range of 18% to 58% compared to the theoretical yield [106]. Meanwhile, genetic modification of PNSB strains has been tried in the recent years, especially on deactivating uptake hydrogenase. For example, it was

found that *hupSL* gene deficient mutant of *Rhodobacter sphaeroides* improved hydrogen production yield compared to the original strain [98, 107]. In a recent study, Wang et al. [108] improved the hydrogen yield up to 45% in photo fermentation by genetically deactivating the Calvin–Benson–Bassham reductive pentose phosphate pathway of *Rhodobacter capsulatus*. Moreover, some chemical compounds were also used to mutagenize PNSB. For example, to overcome the ammonium inhibition on hydrogen production, ethyl methane sulfonate was used to mutagenize *R. sphaeroides* and obtained a glutamine auxotrophic mutant TJ-0803, which can produce hydrogen efficiently from tofu wastewater with ammonium concentration up to 60 mg/L [109]. On the other hand, as shown in Table 2, mixed consortia obtained from different sources were also widely used because of the inexpensive cultivation cost. Moreover, sterilization of the feedstock is usually needed for the pure strain photo fermentation, which also increases the overall cost. Some other researchers also claimed that the consortia can result in higher hydrogen yield with respect to the complex feedstock from waste materials [110]. Therefore, mixed culture obtained from silt sewage, pig manure, and cow dung, etc., were used in different studies [83, 89].

2.2.3 Sequential/combined dark and photo fermentation

On the one hand, the hydrogen yield of single dark fermentation is limited due to the generation of byproducts, i.e. different VFAs. On the other hand, the photo fermentation favours VFAs other than simple sugars. Therefore, integrating the two types of fermentation together provides a solution to waste valorization. A sequential mode, i.e. the waste materials are fed into dark fermentation reactor first, and then the VFA-rich effluent from dark fermentation is used as substrates for photo fermentation, has been proposed [48, 111-113]. In this concept, the optimal condition can be controlled

separately in the two separated reactors, thus not only the hydrogen yield of the substrate is expected to increase, but also the final effluent quality with respect to the COD level should be improved. Numerous studies have been performed with different feedstocks, including different types of wastes, and the results demonstrated the benefit of using the sequential system. Food waste and cassava was used as feedstock to test the new configuration, hydrogen production improvements of 205% and 307% were achieved for food waste and cassava, respectively, compared to the dark fermentation alone [114]. Cheng et al. [54] investigated the hydrogen production efficiency of swine manure through sequential dark and photo fermentation and achieved a hydrogen yield of 247.7 mL H₂/g VS, which was 3.5 times higher compared to only with dark fermentation (71.8 mL H₂/g VS). As shown in Table 3, the prominence of using the sequential system has also been identified with other waste materials, such as sugar beet molasses, corncob, sugarcane bagasse, distilled wastewater, etc. [44, 106, 114, 115]. Recently, pilot scale continuous sequential dark and photo fermentation system was also investigated by Zhang et al. [89]. Hydrolysed corn stover was used as feed stock at organic loading rate of 15 g COD/L. The dark reactor had a working volume of 3 m³ and the photo reactor 8 m³, and the two reactors were operated at different temperature and pH conditions. The results showed an overall high hydrogen yield of 362 mL/g COD with production rate of 7.5 m³/m³/d and 4.7 m³/m³/d for dark and photo reactor, respectively.

Even though the sequential dark and photo fermentation could achieve a high hydrogen yield, the necessity of two separated reactors and the different fermentation conditions make the system complex and expensive. Moreover, the properties of the effluent from dark fermentation is normally not suitable for direct photo fermentation, thus pretreatment is usually needed before being fed into photo reactor. For example, the

final pH after dark fermentation (around 3.5-4.5 if without pH control throughout dark fermentation process) is much lower than the optimal pH (around 7) for photo fermentation [55], and adjustment of the pH should be applied. Therefore, integrating the two fermentation processes into one single reactor to save operational cost attracts researchers' attention. In other words, developing a method to co-culture the dark and photo fermentation bacteria together is important. The complex waste organic matters are firstly degraded by dark fermentation bacteria, then the produced VFAs are consumed *in-situ* by PNSB. However, due to the different optimal conditions of dark and photo fermentation, how to control the environmental condition after integration is always an issue. With a mixed consortium for dark fermentation and *Rhodobacter sphaeroides* for photo fermentation as inoculum, the effect of substrate content, cell concentration, light source and intensity, and also lighting regime were investigated when ground wheat starch was used as feedstock [116, 117]. The authors found that the hydrogen production yield was obtained at a low substrate concentration while the hydrogen production rate was achieved at a high substrate concentration. The hydrogen yield did not always increase along with the cell concentration, and biomass concentration of 1.1 g/L and biomass/substrate ratio of 0.22 were found to be the best. Moreover, among the different light sources, including tungsten, fluorescent, infrared, mixed tungsten and infrared, and halogen lamps, the most suitable one was identified to be halogen lamp. When the light intensity varied from 1 to 10 klux, the highest one yielded the high hydrogen production, while continuous lighting was proved to be better than other different durations of dark/light cycles, such as 0.5/0.5, 2/2, 4/4 hours interval. Chandra and Venkata Mohan [118] studied hydrogen production from synthetic wastewater using a co-culture of two consortia, and the result showed 40% hydrogen yield improvement of the co-culture

fermentation compared to dark fermentation alone. The first continuous feeding combined fermentation study was performed by Argun and Kargi [119] with ground wheat starch as feedstock. An annular-hybrid bioreactor with mixed culture of *Clostridium beijerinckii* (dark fermentation strain) and *Rhodobacter sphaeroides*-RV (photo fermentation strain) at different HRTs (from 1 to 6 days with 1 day interval) was used, and the highest hydrogen yield of 90 mL/g starch was observed at HRT of 6 days. However, the authors claimed that the results were not desirable because even the highest hydrogen yield in the combined system was lower than the single dark fermentation reactors. The main reason was that the operational parameters of the combined dark and fermentation system are usually set close to photo fermentation since PNSB is more sensitive to environmental condition changes compared to dark fermentation bacteria [119]. Thus the fermentation environment was not ideal for dark fermentation bacteria, which resulted in a low production rate in the combined system. Moreover, due to the glucose contained in the substrate, the sugar metabolic pathway of the PNSB was initiated, and it was not easy to alter the VFA metabolic pathway as fast as expected. In another continuous study performed by the same group, after optimization the culture and fermentation condition, a much higher hydrogen yield of 470 mL/g sugar was observed at HRT of 8 days in the single mixed reactor, in which a mixture from anaerobic sludge was used as dark fermentation bacteria and pure *Rhodobacter sphaeroides* was for photo fermentation [120]. This indicated that the culture and HRT played an important role in achieving a high hydrogen yield in the single combined dark and photo fermentation reactor. However, compared to either the individual dark/photo fermentation or the sequential dark and photo fermentation system, the studies of using the combined single dark and photo reactor are much less, especially with waste/wastewater as substrates.

Thus more studies should be performed focusing on optimization of the fermentation conditions using real waste as substrate.

Table 3. Some selected studies of hydrogen production from the sequential/combined dark and photo fermentation.

Reactor type	Waste type	DF culture	PF culture	DF H ₂ yield	PF H ₂ yield	Overall yield	Temperature	pH	Ref
Sequential continuous	Corn stover with enzymatic hydrolysis	Mixed culture	Mixed culture	7.5 m ³ /m ³ /d	4.7 m ³ /m ³ /d	362 mL/g COD	DF: 35; PF: 30	DF: 4.4; PF: 7.0	[89]
Sequential batch	Sugar beet molasses	<i>Caldicellulosiruptor saccharolyticus</i>	<i>Rhodobacter capsulatus hup⁻</i> mutant	4.2 mol/mol sucrose	equivalent to 9.5 mol/mol sucrose	13.7 mol/mol sucrose	DF: 72±1; PF: 30-33	DF: 6.9; Initial PF: 6.7	[106]
Sequential batch	Corn cob with enzymatic hydrolysis	Mixed culture	<i>Rhodobacter sphaeroides</i>	120 mL/g-corn cob	714 mL/g COD	-	DF: 36; PF: 35	Initial DF: 7.0; PF not mentioned	[115]

Sequential batch	Sugarcane bagasse with sulphuric acid, autoclave and enzyme treatment	<i>Enterobacter</i> <i>aerogenes</i> MTCC 2822	<i>Rhodopseudomonas</i> BHU 01	1000 mL/L waste	755 mL/L waste effluent from DF	-	DF: 30; PF: 34	Initial DF: [44] 6.8; PF: 6.8
Sequential batch	Distillery wastewater with pH neutralization and sterilization	Mixed culture	<i>Rhodobacter</i> <i>capsulatus</i> B10 and <i>R. sphaeroides</i> B- 3059	1.6 L/L waste	16 L/L waste	17.6 L/L waste	DF: 37; PF: 30	DF: 5.0; [51] PF: -
Sequential batch	Food waste and cassava	Mixed culture	<i>Rhodobacter</i> <i>sphaeroides</i> ZX-5	Food waste: 220 mL/g substrate; cassava: 199 mL/g substrate	Food waste: 451 mL/g substrate; cassava: mL/g substrate	Food waste: 671 mL/g substrate; cassava: 810 mL/g substrate	DF: 37; PF: 30	Initial DF: [114] 6.8; Initial PF: 7.0

671 mL/g									
substrate									
Combined	Ground wheat	<i>Clostridium</i>	<i>Rhodobacter</i>	-	-	90 mL/g	32 ± 2	7.0-7.5	[119]
continuous	starch	<i>beijerinckii</i>	<i>sphaeroides</i> -RV			starch			
Combined	Acid hydrolyzed	Mixed culture	<i>Rhodobacter</i>	-	-	420 mL/g	30 ± 1	Initial pH:	[120]
continuous	waste wheat		<i>sphaeroides</i>			starch		7.0	
	starch								
Combined	Synthetic	Mixed culture	Mixed culture	-	-	Not clearly	30	Initial pH:	[118]
batch	wastewater					mentioned,		6.0	
						but 40%			
						improvement			
						compared to			
						DF alone			

Combined	Potato juice with	<i>Clostridium</i>	<i>Rhodospseudomonas</i>	-	-	6.4 ± 1.3	30	pH Buffer [118]
batch	addition of	<i>butyricum</i>	<i>palustris</i>			mol/mol		of 7.6
	glucose					glucose		

*Some abbreviations: MBT: Mechanical-biological-treatment; OFMSW: Organic fractions of municipal solid waste; CSTR: Continuously stirred tank reactor; UASB: Upflow anaerobic sludge blanket reactor; VS: Volatile solid; COD: Chemical oxygen demand.

2.3 Thermochemical gasification

Biohydrogen can also be produced through gasification of biowaste. Gasification is a partial oxidization process of the organic feedstocks at high temperatures and sometimes at high pressure (i.e. hydrothermal gasification), aiming to produce syngas (H_2 , CO , CH_4 and CO_2). Several by-products can also be found in this process, such as light hydrocarbons, biochar, tar, etc. [121]. The hydrogen concentration and production among the produced syngas varies from case to case, but it can be improved by optimizing the reaction parameters, which will be discussed in the next section. The main reactions during gasification process are shown in Eq. (12-18).

As shown in Fig. 7, different types of prevalent gasification for hydrogen production have been reported in these years, such as hydrothermal gasification, air gasification, steam gasification, and two-stage pyrolysis–gasification system. Moreover, the specific plasma gasification with either air or steam as agent were also reported. The hydrothermal gasification has been applied into hydrogen production from high moisture content organic waste [122], while the other four types are usually used for waste with a relatively

low water content. Hydrothermal gasification is a thermochemical process that uses hot and compressed water under critical or near-critical conditions (374.3 °C and 22.1 MPa) to reform biomass [123]. The air gasification is achieved through partial oxidation with air or oxygen-enriched air, but the yield and heating value of the produced gases are quite low due to the dilution of atmospheric nitrogen [124]. Steam gasification was reported to be one of the most promising hydrogen producing approaches since it generates hydrogen with high efficiency and concentration due to the extra hydrogen element provided by the steam and the low carbon footprint of this process [125, 126]. The plasma gasification is different from other gasification because of the heat source (i.e. plasma) from the external power, and the generated plasma arc torches can create an electric arc and plasma gas up to 15000 °C; while the gasification agent can be air, oxygen or steam [127]. The two-stage pyrolysis–gasification system is easier to control for high yield of hydrogen, particularly from plastic wastes, because the gases generated in pyrolysis is further reformed by steam gasification to produce hydrogen with the help of catalysts [128].

Fig. 7. A schematic diagram of different types of gasification: a) hydrothermal gasification, b) air or steam gasification, c) two-stage pyrolysis–gasification system.

Adapted and modified with permission from [129-131]. Copyright (2019), American Chemical Society; Copyright (2019), Elsevier.

2.3.1 Different feedstocks of gasification

Gasification is a promising technology to convert the organic wastes into hydrogen in a fast decomposing process. Almost all kinds of organic wastes including forest and agricultural biomass, municipal solid waste, sewage sludge, food waste, and animal manure, have been tested as the feedstock in gasification to produce hydrogen. As shown in Fig. 8 about different feedstock for gasification in the past ten years, it shows that wood waste and municipal solid waste are the top two waste streams that were fed into gasification, which is mainly because of the low water content of wood waste and the abundance and easy accessibility of the municipal solid waste. Besides, sewage sludge, plastics, agricultural residual and food waste have also been widely investigated.

Fig. 8. The number of publications about gasification of different waste materials in the past ten years (2009-2018). The data source comes from “Scopus database”.

2.3.2 Operational parameters of gasification

The hydrogen production during gasification varies significantly with the different operational parameters, such as feedstock property, reaction temperature, gasification agent, selected catalyst, etc. Thus in order to increase the hydrogen production and concentration, optimization of these operational parameters have been investigated.

First of all, the different characteristics of the waste influence the hydrogen production significantly. It is reported that cellulose and lignin play an important role in determining the hydrogen production and a higher content of cellulose and lignin yields more gaseous products and hydrogen [132]. For example, Chang et al. [133] found that the hydrogen yield from bagasse gasification (up to 29.72 g H₂/kg substrate) was higher than the one from mushroom waste (up to 19.78 g H₂/kg substrate), which was mainly due to the higher cellulose and lignin content in bagasse compared to mushroom waste. Besides, the moisture content, alkali content and particle size of waste were also correlated to the hydrogen production of gasification [134, 135]. Shie et al. [136] reported that the H₂ content increased along with the moisture content of the feedstock. The similar results were also found by Nanda et al. [129] that the hydrogen yield of hydrothermal gasification with water-to-feedstock ratio (W/F) of 10 was almost two times higher than the yield at W/F of 5. Moreover, the same authors also found that when the alkali content (K₂CO₃) in the feedstock increased from 1% to 2%, the hydrogen yield also increased from 5.78 g/kg to 9.56 g/kg. On the other hand, feedstock with larger particle size possessed greater resistance of heat transfer, resulting in incomplete decomposition, while the reduction of particle size contributed to the improvement of carbon conversion efficiency and hydrogen yield [135, 137].

Another important factor influencing the hydrogen production of gasification is the reaction temperature. In case of different gasification technologies, the reaction temperatures are different. As shown in Table 4, the temperature of hydrothermal gasification is generally between 300 to 600 °C; while in terms of air and steam gasification, the temperature usually ranges from 700 to 1000 °C. Whereas the temperature can reach as high as 2000 °C in the plasma gasification [138]. In general, the higher temperature usually leads to more effective destruction of the feedstock, consequently results in a higher hydrogen yield [132, 139, 140]. For example, the hydrogen yield elevated from 28.86 to 77.20 g/kg with the temperature increased from 750 to 950 °C in the steam gasification of municipal solid waste [141]. However, it was also reported that when the temperature was above 1000 °C in the plasma gasification, the hydrogen yield decreased with the increase of the reaction temperature [138], which suggested that the hydrogen generation reaction was not favoured when the temperature was too high (>1000 °C).

Gasification agent ratio is another important parameter for the hydrogen production. The W/F ratio in hydrothermal gasification was reported to have a positive relationship with the hydrogen yield [129, 142]. However, higher W/F ratio also means higher energy consumption to reach the reaction point, thus an input and output energy efficiency should be carefully considered. Besides, a small amount of oxidant, such as H_2O_2 and KMnO_4 , was found to promote the hydrogen production in hydrothermal gasification, while excess oxidant may lead to the oxidation of H_2 [143, 144]. Equivalence ratio (ER), which was defined as the amount of available air per kilogram of feedstock, was investigated by Zhang et al. [145] in air gasification of municipal solid waste, and the results showed that the hydrogen yield increased from 12.04 to 18.88 g/kg when the ER were increased from

0.08 to 0.12. However, an excessive ER may also lead to the reduction of the hydrogen yield, because the reaction can transit to a complete combustion with excess air [133]. Compared to using air as agent, steam was reported to enhance the performance of hydrogen production significantly [133]. Sheth and Babu [146] increased the steam flow from 0.11 to 0.58 kg/h when wood waste was used as feedstock, and the highest hydrogen yield of 21.58 g/kg was detected at the steam flow of 0.31 kg/h. This is explained by that low steam to feedstock ratio led to the formation of carbon and methane while high ratio enhanced hydrogen formation [132]. However, with excess amount of the steam in the reactor, the yield of hydrogen decreased because the overall recovered energy was lost for heating the steam [132, 133].

In order to improve the hydrogen yield, many different catalysts were prepared and employed in the gasification process. The proposed mechanism of catalytic gasification was introduced and summarized by Arnold and Hill [147] in a recent publication indicating that 1) the catalyst can adsorb the gasifying agent and accelerate the reaction at the catalyst-carbon interface [148]; and 2) the catalyst particles can be deposited at different sites on the carbon surface and act as “carbon worm” to eat and release the carbon that could react with the gasifying agent rapidly [149]. The alkali salts, such as NaOH, KOH, $\text{Ca}(\text{OH})_2$, Na_2CO_3 , K_2CO_3 and NaHCO_3 , were found to be efficient in enhancing hydrogen production in hydrothermal gasification [144, 150]. For example, the hydrogen production from food waste was improved by adding NaOH, KOH and $\text{Ca}(\text{OH})_2$, and NaOH was reported to have the best performance [150, 151]. Other researches also reported that the alkali materials can promote the hydrogen generation and inhibit char and CO formation in the water-gas shift reaction of hydrothermal gasification [152, 153]. On the other hand, the prevalent catalysts employed in the

gasification other than hydrothermal process were dolomite, nickel, alumina, and cerium based catalysts. These catalysts can provoke the water-gas, CO shift, steam methane reforming and tar destruction, and consequently contribute to the improvement of hydrogen yield [132]. The amount of Ni in the Ni/CeO₂/Al₂O₃ catalyst was investigated for hydrogen production from waste tyres in a pyrolysis–gasification process [154], and the results showed a positive impact on hydrogen production with the increased amount of Ni. A newly developed tri-metallic catalyst (nano-NiLaFe/ γ -Al₂O₃ catalyst) was proved to enhance the hydrocarbons and tar cracking, and the hydrogen production was higher when the new catalyst was used compared to the traditional dolomite catalyst [155].

2.3.3 High hydrogen content through reforming and purification

The hydrogen production yield can be optimized by adjusting the operational parameters as discussed above. However, the syngas composition is still complex and not stable, as well as the gasification byproducts. Thus to increase the hydrogen concentration, focuses were also put on optimizing the gasification products, i.e. reforming of the syngas and tar, and purification of the syngas. The commonly used reforming technologies include steam reforming and catalyst reforming [156]. As for steam reforming, CO is typically reacted with steam to produce hydrogen and CO₂, and it was reported that the hydrogen concentration can be significantly elevated by more than 80% dry base with steam reforming according to the thermodynamic calculations [157]. The steam reforming includes the water-gas shift reaction that consists of two main steps: a high temperature step (320-360 °C) aiming on fast reaction and a low temperature step (190-250 °C) targeting on high conversion rate [158]. Moreover, a high pressure and steam-to-carbon ratio also can result in high CO conversion and reaction rate. Catalyst is usually needed in the water-gas shift reaction, and the catalyst activity can be optimized through

a high temperature condition with a good steam management [159, 160]. Recently, researches on using new materials in secondary reformer to produce hydrogen with tars removing were also performed. For example, a novel reformer with porous ceramic was developed, which led to a considerable increase in the hydrogen content from 33.4% to 48.5% and the content of CO, CH₄ and C₂-C₃ compounds decreased [161].

Although the high yield and high concentration of hydrogen can be obtained after the reforming, the reformed syngas still needs to be purified due to the large quantity of CO₂, and some other unconverted or partly converted impurities (such as CH₄, CO, H₂S, N₂ and/or Ar, etc.). For hydrogen purification, many technologies have been developed in these years including the swing adsorption, selective membranes and cryogenic/low-temperature processes. As for swing adsorption, three different types have been proposed: pressure swing adsorption (PSA), electric swing adsorption (ESA) and temperature swing adsorption (TSA), among which the PSA was found to be the most prevalent one due to its low energy penalty and high separation efficiency [158]. The polymeric membrane is one of the most mature hydrogen selective membrane, but its application is still limited because it is only suitable for low temperature process and vulnerable to impurities such as HCl, SO_x and CO [162, 163]. In order to overcome the shortcomings of polymeric membrane, high-temperature hydrogen selective membranes, such as metallic membrane, microporous ceramic membrane, porous carbon membrane, and dense ceramic membrane, were extensively investigated [163], among which metallic membrane showed its potential due to the high purified ability (99-99.995%) [158]. In addition, the cryogenic/low-temperature separation is another method to separate hydrogen from syngas according to the different boiling points of the different compounds of the syngas. When syngas is cooled down to cryogenic temperatures (-150 °C), the hydrogen remains

in gas phase while the impurities are condensed, which makes the hydrogen easy to separate. However, the application of this technology is limited owing to the high refrigeration demand and low hydrogen purity (81-83%) compared to other purification method mentioned above [158, 164].

Table 4. Summary of gasification technologies for waste-to-hydrogen

Gasification type	Reactor type	Waste type	Size (mm)	Catalyst type	Ratio (wt.%)	Temperature (°C)/Pressure (MPa)	ER	Agent ration	H ₂ yield (g/kg)	Ref
Hydrothermal gasification	Batch autoclave	Food waste	-	Alkali catalysts	6.67	330 /13.5	0.28	-	4.14 -26.5	[150]
	Batch autoclave	Wood residue	≤0.5	K ₂ CO ₃	10	500-600/ 20.0-42.5	-	-	17.4-52.2	[165]
	Batch autoclave	Cow dung	-	Ca(OH) ₂	-	400/26-27	-	-	0.2-1.4	[166]
	Batch autoclave	Fruit waste	≤0.5	NaOH, K ₂ CO ₃	1-2	400-600/ 3- 25	-	W/F:5, 10	0.16-9.56	[129]
	Continuous fluidized bed reactor	Sewage sludge	-	Alkali catalysts	0.1- 0.9	480-540/25	-	W/F:5	3.0-30.98	[167]

Air gasification	Continuous	Bagasse	≤ 0.35	-	-	700-900	0.29-	-	3.64-29.72	[133]
	feeding						0.34			
	gasifier									
	Continuous	Mushroom	≤ 0.35	-	-	700-900	0.27-	-	5.02-19.78	[133]
	feeding	waste					0.33			
	gasifier									
	Continuous	Municipal	-	-	-	1000	0.08-	-	12.04-18.88	[145]
	plasma	solid waste					0.12			
	gasifier									
Steam	Continuous	Municipal	-	-	-	1000	0-	0-100 kg/h	19.78-31.47	[145]
gasification	feeding	solid waste					0.12			
	plasma									
	gasifier									

Continuous feeding gasifier	Mushroom waste	≤ 0.35	-	-	700-900	-	S/F: 0.5	6.20-40.46	[133]
Continuous feeding gasifier	Municipal solid waste	≤ 5.0	Dolomite	-	750-950	-	S/F: 0.77	28.86-77.20	[141]
Batch gasifier	Wood waste	≤ 25.4	-	-	800-900	-	SS: 0.11-0.58 kg/h	6.29-21.58	[146]
Batch gasifier	Sewage sludge	-	-	-	700-1000	-	SS: 3.0 g/min	27-84	[168]
Continuous feeding gasifier	Municipal solid waste	≤ 5	tri-metallic catalyst	-	750-900	-	S/F: 0-2.67	39.75-126.02	[155]
Continuous feeding gasifier	Municipal solid waste	≤ 5	NiO/MD, NiO/ γ - Al_2O_3	-	700-800	-	S/F: 0-3.08	21.9-98.15	[169]

	Batch gasifier	Saw dust	0.43–0.50	CaO	0-2	670-710	-	0.58-1.58	26.97-61.49	[170]
Two-stage pyrolysis– gasification system	Batch two- stage reactor	Waste plastic	≤5.0	Ni–Mg–Al catalyst	0-2.0	600-900	-	SS:1.9-14.2 g/min	140-380	[171]
	Batch two- stage reactor	Polypropylene	≤2	Ni/Al ₂ O ₃	-	600-800	-	SS: 0-4.74 g/h	33-69	[130]
		polyethylene			-		-		33-92	
		Polystyrene			-		-		27-74	
	Batch two- stage reactor	Biomass and plastic mixtures	≤0.2	Ni/Al ₂ O ₃	-	600-800	-	4.74 g/h	39.90-54.54	[172]
	Batch two- stage reactor	Waste tyres	≤6	Ni/CeO ₂ /Al ₂ O ₃	0.5	500-800	-	-	67-80	[154]

Note: ER: equivalence ratio, representing the amount of available air per kilogram of feedstock; W/F: water-to-feedstock ratio; S/F: steam-to-feedstock ratio; SS: steam speed.

2.4 Microbial electrolysis cells

MEC is a relatively new hydrogen-producing technology compared to fermentation and gasification, which was proposed almost at the same time by two individual groups about 15 years ago [173, 174]. The MEC system is mainly consisted of two electrodes: anode and cathode. As shown in Fig. 9, the two electrodes can be either in the same chamber, so-called single-chamber MEC, or separated into two chambers, so-called two-chamber MEC. At the beginning stage of MEC, more researches were performed with two-chamber system, because it resulted in high purity of hydrogen and also avoided the interference of the two electrodes [175]. Moreover, it is also convenient to control and/or optimize the working condition of the hydrogen-production electrode/chamber, i.e. cathode chamber. In order to separate the two chambers, membrane is needed, and the most commonly used membrane is proton exchange membrane. In recent years, other membranes were also investigated, including cation/anion exchange membrane, charge-mosaic membrane and bipolar membrane [24]. In two-chamber MEC, the organic wastewater is fed into the anode chamber, while different solutions can be used in the cathode chamber, such as phosphate buffered solution, moderate acidified water, salt solutions and bicarbonate buffers etc. [176, 177]. However, due to the high cost and potential loss of the membrane, the configuration of MEC has been modified and membrane-free single-chamber MEC has been proposed and widely applied in these years. No matter one or two chambers, the main working concept is the same that the organic matters are oxidised in the anode to generate electrons, and the electrons are transported to the anode and consequently to the cathode and being accepted by the protons in the cathode to generate hydrogen. Moreover, it must be mentioned that the MEC is also an anaerobic system that is sensitive to oxygen. Taking acetate as an example,

the main chemical reactions occurring in the MEC are shown in Eq. (19-21). The reduction of protons is a thermodynamically non-spontaneous process, thus an external power is needed to drive the reaction. Compared to the conventional water electrolysis where 1.2-3.5 V is required, the MECs normally needs a lower voltage between 0.2 to 0.8 V [24]. Apart from using a battery as the external power source, other more sustainable power sources are also proposed, such as power generated from microbial fuel cells, solar and wind energy, waste heat from other facilities [15, 178].

Fig. 9. A schematic diagram of MEC for hydrogen production: a) two-chamber MEC and b) single-chamber MEC. Adapted and modified with permission from [15] and [179]. Copyright (2019), Elsevier.

2.4.1 Different waste streams

The hydrogen production based on MEC system has become a hot topic and a huge number of studies have been performed since the first publication. The majority of the studies were conducted with pure chemical solutions as substrates, such as acetate, butyrate, glycerol, glucose, etc. However, the physic-chemical composition and properties (such as pH, conductivity, etc.) of the real wastes are more complex compared to synthetic medium, which might influence the performance of MEC significantly different. For example, Cotterill et al. [180] claimed that the energy efficiency and COD removal rate performed better with synthetic waste than the real waste. Therefore, more attentions should be paid on the research of real waste streams. As shown in Table 5, the waste streams fed in MECs mainly include effluent from fermentation and/or anaerobic digestion process and different types of wastewater, such as domestic wastewater [175, 181, 182], livestock farming wastewater [183, 184], industrial wastewater [185, 186], waste activated sludge [187, 188] etc. Due to the complex characteristics of different waste streams, the hydrogen production efficiency and MEC performance varied significantly from waste to waste. For example, wastewater from chemical industry and food processing factory were investigated in identical single-chamber MECs, respectively. The results showed that chemical industrial wastewater had a higher hydrogen production rate (0.58 L/L/d) compared to food process wastewater (0.35 L/L/d); while food processing wastewater had a much higher hydrogen concentration (86%) compared to chemical industrial wastewater (32%) [185]. Combining dark fermentation and/or anaerobic digestion together with MECs [186, 189, 190], i.e. using MEC technology to produce hydrogen from effluent/residuals of dark fermentation and anaerobic digestion, has also been investigated, and the results demonstrated an improvement of hydrogen production efficiency and consequently an overall energy recovery efficiency. For

example, an integrated system of dark fermentation and two-chamber MEC was used to recover hydrogen from sugar beet juice wastewater, and an overall hydrogen yield of 6 mol/mol hexose was achieved [186]. Moreover, by integrating dark fermentation and single-chamber MEC together, an overall hydrogen recovery efficiency of 96% was obtained with molasses wastewater as substrate [190].

2.4.2 Operational parameters of MEC system

Since the discovery of MEC, a lot of researches have been conducted to optimize the system efficiency to increase the hydrogen production efficiency, through manipulating different operational parameters, such as temperature, electrodes with different materials, suppressing other microorganism activities besides exoelectrogens etc.

Hydrogen can be produced from treating wastewater in MEC system at a wide temperature range, which has been identified as one of the most attractive advantages compared to other hydrogen producing system. The exoelectrogens activity was observed when temperature ranged from 5-45 °C [191], and an efficient hydrogen production was also reported from molasses wastewater using single-chamber MEC under 9 °C. Heidrich et al. [175] investigated pilot scale MEC treating domestic wastewater in England and stated that the influence was insignificant when ambient temperature varied between 13.5 and 21.0 °C during June to September. However, in a recent pilot scale MEC field study, domestic wastewater was treated in MEC at ambient temperature (1-22 °C) throughout a year [192]. The results showed that hydrogen production continued all the year around, while the production efficiency presented a positive relationship with the temperature, which mainly because the activity of the exoelectrogens increased along with the temperature. Thus most of the studies performed in the lab scale, the temperature was controlled at a moderate condition from 20-35 °C in order to achieve a high hydrogen

production efficiency. However, due to the energy consumption of keeping the temperature constant, the trade-off between the recovered energy (i.e. hydrogen) and the input energy should be carefully addressed.

The external power supply influences the current density and reaction time of MEC system, which plays an important role in determining the hydrogen production efficiency, including rate and yield. Shen et al. [183] used a two-chamber MEC to treat wastewater from hydrothermal liquefaction of swine waste with the external voltage ranging from 0.4 to 1.2 V with an interval of 0.2 V. The results showed an improvement of hydrogen production efficiency, as well as coulombic efficiency, along with the increase of the external voltage, evidenced by that the production rate increased from 13 to 168 mL/L/d and the production yield also increased from 0.58 to 5.14 mmol/g COD. Moreover, the effluent from dark fermentation of molasses wastewater was used to produce hydrogen through single chamber member-free MEC with an increasing external voltage from 0.2 to 0.8 V with the unit of 0.1 V [190]. The hydrogen production rate demonstrated an increasing trend along with the increasing voltage up to 1.52 L/L/d. However, the authors also mentioned that the hydrogen production increasing rate was not significant when the voltage was above 0.6 V. Moreover, the highest overall energy efficiency was observed at external voltage at 0.6 V, instead of the highest external voltage of 0.8 V. The same phenomenon was also observed by Feng et al. [188] who claimed that the hydrogen production yield increased with the applied voltage from 0.3 to 0.6 to 1.2 V, whereas the net energy output was only obtained with voltage at 0.3 and 0.6 V. Therefore, it seems that the higher external voltage applied, the higher amount of hydrogen produced from MEC. However, if taking other parameters (such as energy recovery efficiency, coulombic efficiency, etc.) into consideration, the optimal applied external voltage is

highly influenced by the characteristics of the used substrate, such as the conductivity, COD levels, etc.

The electrode material and/or special pretreatment of both anode and cathode are important for achieving a high substrate utilization rate and hydrogen production rate. As shown in Table 5, the most commonly used electrode material was carbon-based material, including carbon cloth, carbon felt, carbon nanotubes, carbon brushes, graphite plates, graphite fibres, etc., which is mainly due to their low cost, good conductivity, and high versatility of morphologies. Other non-carbon materials, such as copper, Fe tube and stainless steel, were also investigated in these years. In order to improve the performance of anode, pretreatment including ammonia gas treatment and heat treatment were proposed to be conducted [193]. On the other hand, it was observed that the hydrogen evolution reaction (HER) with only plain carbon electrode was slow, thus catalyst is usually used to minimize the overpotential of HER to drive a fast hydrogen formation process [25]. Currently, Platinum (Pt) has become the most commonly used catalyst coated on cathode electrode and exhibited high efficient performance [194]. Due to the expensive cost of precious platinum, different alternatives, such as stainless steel, molybdenum disulfide (MoS_2), nickel alloys, microbial biocathode, etc., were also investigated in recent years in treating real waste streams [25, 194]. For example, Tenca et al. [185] compared the performance of cathode with Pt, MoS_2 and stainless steel, respectively, in treating chemical industrial and food processing wastewater, which demonstrated that MoS_2 was a good candidate in replacing Pt in terms of energy recovery. Hydrogen yield from waste activated sludge (90.6 mL/g VSS) based on cheap electrodes (Fe tube anode and graphite pillar cathode) was reported by Feng et al. [188] to be comparable and even higher than the Pt cathode (52.2 mL/g VSS in [195]; 63.5 mL/g

VSS in [196]; 95.2 mL/g VSS in [197]). Moreover, the high catalytic activity of nickel foam cathode was also identified in hydrogen production from hydrothermal liquefaction wastewater [183].

Another important factor that influences the hydrogen production efficiency in MEC system is the rapid growth of methanogens, which results in methane production, instead of producing hydrogen [198, 199]. This usually happens after a long-term operation, and becomes one of the most serious challenges that needs to be considered during the operation of MEC. In single-chamber MEC, the produced hydrogen could be consumed by the hydrogenotrophic methanogens and drop the overall hydrogen production; while in two-chamber MEC, the growth of methanogens in anode chamber limited the production of electrons that should be transferred into cathode to generate hydrogen. For example, effluent from dark fermentation of corn stover lignocellulose was used to produce hydrogen in a single-chamber MEC, more than 10% of methane was detected in the produced gas [200], which resulted in further energy input to purify the gas. Moreover, Cusick et al. [181] investigated hydrogen production of winery wastewater using small-scale (working volume 28 mL) MEC in batch mode, the results showed a high hydrogen concentration (around 70%) and yield (291 mL/g COD). However, when they upgraded the system into pilot scale (working volume 910 L) in continuous mode, the results were not desirable because hydrogen production was only detected at sub-mesophilic (15-22 °C) condition at the beginning days followed by the failure of producing hydrogen and supplemented by high methane production (0.24 L/L/day with concentration of 86% and the rest is CO₂) [201]. Therefore, inhibition on the activity of the methanogens in MEC system is necessary to achieve a high purity of hydrogen, and different methods have been proposed in these years [190, 199, 202-205], which mainly include using pure

exoelectrogens to avoid the interference of methanogens, adding chemicals with the ability of inhibiting methanogens (e.g. 2-Bromoethanesulfonate, 2-chloroethanesulfonate, neomycin sulfate, etc.), changing different operational conditions (e.g. low temperature, exposure to oxygen, different external voltage, etc.) and other treatment that leads to inhibit methanogens (e.g. ultraviolet irradiation). For example, Lu et al. [190] examined the different external voltage (0.2-0.8 V) impact on the methane production and concentration in the final produced gas, and reported that by applying a relatively higher external voltage could effectively inhibit the methane generation. Operating the MEC treating molasses wastewater at temperature of 9 °C, no methane was detected throughout the whole experiment [204].

2.4.3 Microorganisms involved in MEC

As mentioned above, the organic matters in the waste are oxidised in the anode chamber to generate electrons that being transferred to the anode and consequently to the cathode to be used to generate hydrogen. Thus, the microorganism in the anode in MEC is of great importance to achieve an efficient hydrogen production. The microorganisms that are capable to transfer the electrons from the chamber to the anode are called exoelectrogens. However, even though some exoelectrogens have been isolated, in most of the available studies, mixed culture containing exoelectrogens was used [206, 207]. The consortium was enriched in microbial fuel cells to form a biofilm in the anode, and then the reactor configuration was modified to be a MEC. Currently, the most well-known exoelectrogenic groups are *Geobacter* spp. and *Shewanella* spp., among which the most studied species are *Geobacter sulfurreducens* and *Shewanella oneidensis*. The detailed working mechanism of the two species was described by Kumar et al. [208] and not repeated in this study. Recently, some other exoelectrogenic species were also reported

and isolated from different MEC systems [206, 209], such as *Sphingomonas* strain DJ, *Acetobacterium woodii*, *Rhodoferrax ferrireducens*, *Rhodopseudomonas palustris*, *Ochrobactrum anthropic*, etc. Moreover, in a recent study under alkaline condition, *Alkalibacter* sp. was highly suspected to be a new exoelectrogen working in alkaline MEC system [210]. To sum up, MEC is a relatively new technology compared to other biohydrogen technologies, thus the microorganism related working mechanism is still not clear enough. With the increasing development of biotechnological method, such as high-throughput sequencing technology, more fundamental research revealing the unknown exoelectrogens should be performed in the future [211].

Table 5. Some selected studies of hydrogen production from MECs.

Reactor type	Waste info	Anode	Cathode	External voltage (V)	Temperature (°C)	pH*	CE (%)	Hydrogen yield/rate	Ref
Two-chamber MEC, 500 mL for anode and 1000 mL for cathode chamber	Hydrothermal liquefaction wastewater of swine waste	Carbon felt embedded in activated carbon granules with a titanium nanowire	Nickel foam	1.2	25±2	Initial at 7	11.0	5.14 mmol/g COD	[183]
Two-chamber MEC, 290mL for anode chamber, not mentioned for	Hydrothermal liquefaction wastewater of cornstalk	Carbon nanotubes	Carbon fiber felt	1.0	25±2	Initial at 7	7.0	3.92 mL/L/d	[212]

Cathode									
chamber									
Pilot-scale 120 L reactor with six two-chamber cassettes	Domestic wastewater	Carbon felt	Stainless steel wire wool	1.1	ambient temperature varying from 13.5 to 21.0	Influent at 55.0 ± 17.5	7.0 ± 0.4	15 mL/L/d, i.e. 1.49 mmol/g COD	[175]
Two-chamber MEC, the working volume was not mentioned	Effluent from dark fermentation of sugar beet juice wastewater	Carbon fiber integrated with stainless steel	Stainless steel mesh	0.4	25	7.2	70 ± 6	Overall yield from the integrated fermentation and MEC system: 6 mol/mol hexose; while from MEC: around 306 mL/g COD	[186]

Two-chamber MEC, 250 mL for both anode and cathode chamber	Raw waste activated sludge (R-WAS); Alkaline- pretreated waste activated sludge (A-WAS)	Graphite brush Carbon cloth with Pt	0.6	19±1	7.0	R- WAS: 28±10; A- WAS: 34±4	R-WAS: 63.5±6.8 mL/g VSS; A-WAS: 168.9±12.8 mL/g VSS	[196]
Single-chamber MEC with working volume of 2L	waste activated sludge	Fe tube Graphite pillar	0.6	20	7.0 ± 0.2	10.4	90.6 mL/g VSS	[188]
Single-chamber MEC with working volume of 28 mL	Chemical industrial wastewater (IN); food	Heat-treated graphite fibre brushes	Carbon cloth with Pt	0.7	30	For IN: 6.4; For FP: 7.3.	For IN: 10 For FP: 35 IN-Pt: 0.58 L/L/d FP-Pt: 0.35 L/L/d	[185]

processing									
wastewater (FP)									
Single-chamber MEC with working volume of 26 mL	buffered dark-fermentation effluent	Carbon fiber brush	Carbon cloth containing a Pt catalyst	0.6	25	6.7-7.0	87	1.41 L/L/d	[190]
single-chamber MEC with working volume of 90 mL in continuous mode	domestic wastewater	Graphite felt	Carbon paper coated with Ni as catalyst	1.0	30	6.7	-	1.41 L/L/d, i.e. 725 mL/g COD	[182]
Single-chamber MEC with	Effluent from fermentation of corn stover	Ammonia gas treated	Flat carbon cloth containing a Pt catalyst	0.5	-	7.2	-	750 ± 180 mL/g COD	[200]

working volume		graphite fibre								
of 28 mL		brushes								
Single-chamber	Domestic	Ammonia gas	Carbon cloth	0.9	30	DW: 7.4	DW:	DW: 560 ± 112	[181]	
MEC with	wastewater	treated	with Pt			WW: 7.2	64	mL/g COD		
working volume	(DW); winery	graphite fibre					WW:	WW: 291.2 ± 44.8		
of 28 mL	wastewater	brushes					50	mL/g COD		
	(WW)									
Single-chamber	Swine	Graphite fibre	Carbon cloth	0.5	30	6.8	70	1.0 ± 0.1 L/L/d	[184]	
MEC with	wastewater	brushes	with Pt							
working volume										
of 28 mL										

*The pH of the two-chamber MEC showed in this table was the pH in the anode chamber.

**Some abbreviations: VSS: Volatile suspended solid; COD: Chemical oxygen demand; CE: coulombic efficiency.

3 Environmental impacts analysis of biohydrogen from waste

As discussed in the previous section, different types of waste were used to generate biohydrogen through different technologies. It was reported that the biohydrogen-based economy can contribute to reducing the GHG emission, improving the local district pollution, and finally achieving a carbon neutral society. With the increased interest on hydrogen economy, evaluation of the environmental performance of the biowaste to biohydrogen technologies from the whole life cycle perspective is of great importance. Life cycle assessment is a well-established scientific method to quantify the potential environmental impacts by taking all the input (energy, materials, water, etc.) and output (products, emissions, energy, etc.) into consideration [213]. Moreover, LCA can also be used to analyse the weakness and hotspot of each technology, and thereafter assist the decision-making for technology developers, policy-makers and entrepreneurs. Therefore, a lot of LCA studies about hydrogen production from biowaste/wastewater via different technologies have been performed in the past years. The current study will focus on reviewing the LCA studies of fermentation, gasification and MEC system, aiming to summarise the state-of-the-art in the biowaste to biohydrogen field.

3.1 Life cycle assessment

According to the international standard ISO14040 and ISO14044 published on 2006 [214, 215], a life cycle assessment study consists of four stages: 1) the goal and scope definition; 2) the life cycle inventory analysis; 3) the life cycle impact assessment; and 4) the life cycle interpretation. In the first stage, it mainly includes the reason for conducting this study, the potential audience, the system that is going to be studied and the system boundaries, the functional unit, the decision of allocation procedures and life cycle impact assessment methodology, etc. Data collection is done in the second stage, which includes

the input and output of the system defined in the first stage, such as energy, raw materials, emissions to gas/water/soil, etc. During the third stage, the calculation of different impact categories, such as global warming potential, eutrophication potential, and ozone depletion, etc., need to be performed based on the chosen life cycle impact assessment methodology decided in the first stage, such as ReCiPe, IPCC, CML methodology, etc. Whereas in the last stage, the inventory data and/or the impact results are compared and discussed, followed by conclusions and recommendations. Moreover, sensitivity and uncertainty analysis were also suggested by ISO14040 and ISO14044. Therefore, the following review will also try to identify how the previous LCA studies aligned with the ISO guidelines.

Table 6. LCA studies of hydrogen production from waste and wastewater through fermentation, gasification and MEC since 2009.

Technology	Reactor type	Feedstock	System boundary	Functional unit	LCIA methodology	Impact category	Software	Data source	Sensitivity/ Uncertainty	Ref
Fermentation	SDPF	Potato steam peels	Cradle-to- gate	1 kg of H ₂ produced	Eco-indicator 99	Average weighting of damage categories: HH, EQ, RD	SimaPro	Ecoinvent, literature, AspenPlus simulation	Yes/No	[216]
Fermentation	SDPF	Potato steam peels, sweet sorghum stalk, wheat straw	Cradle-to- gate	460 ton H ₂ produced	IMPACT 2002+	Normalized result in “Pt” based on HH, EQ, CC, RD	SimaPro	Ecoinvent, literature, experiment	Yes/No	[217]
Fermentation	DF	Microalgae	Cradle-to- gate	1 MJ of H ₂ produced	Inventory analysis without assessment	CO ₂ emission	-	SimaPro database, experiment	No/No	[218]

Fermentation	DF	Microalgae	Cradle-to- gate	1 MJ of H ₂ produced	Inventory analysis without assessment	CO ₂ emission	-	SimaPro database, experiment	No/No	[219]
Fermentation	DF	Microalgae	Cradle-to- gate	Two types: 1). 1 g microalgae; 2). 1 MJ of H ₂ produced	Carbon footprint	GHG	-	Ecoinvent, experiment	No/No	[220]
Gasification	Air/Steam	Municipal solid waste, wood chips, refuse- derived fuel, scrap tyres	Cradle-to- gate	1 ton produced syngas with fixed H ₂ content	EDIP 2003	GWP, AP, EP, POF	Gabi	Literature	No/No	[221]
Gasification	Air/Oxygen	Switchgrass	Cradle-to- grave	1 km distance of	Inventory analysis	GHG	-	Literature	No/No	[222]

				scooter/fuel						
				system						
Gasification	Steam	Wood	Cradle-to- gate	1 kJ of biomass at the inlet of the installation	IPCC2007	GWP	-	Literature, model simulation	No/No	[223]
Gasification	DG and CFBG	Pine wood	Cradle-to- grave	1 MJ/s of H ₂ production rate	-	GHG CED	-	Literature	No/No	[19]
Gasification	Steam	Wood chips	Cradle-to- gate	1 kg of H ₂ produced	IPCC2007	GHG	-	Ecoinvent, literature	No/No	[224]
Gasification	Steam	Short rotation forestry poplar trees	Cradle-to- grave	200 km at nominal full load	CML2000	ADP, GWP, ODP, POF, AP, EP,	SimaPro	Ecoinvent, literatures,	No/No	[225]

						HTP, FWAE, MAE, TE	AspenPlus simulation			
Gasification	-	Four different lignocellulosic wastes: pine, vine pruning, eucalyptus, almond pruning	Cradle-to- gate	1 Nm ³ of hydrogen	CML2001	GWP, AP, EP	Gabi	Ecoinvent, literatures,	No/No	[226]
Gasification	Air, DFBG	Poplar chips	Cradle-to- gate	1 kg of H ₂ produced	CML2001	ADP, GWP, ODP, POF, AP, EP, LC	SimaPro	Ecoinvent, literatures, AspenPlus simulation	No/No	[227]
Gasification	Steam, DFBG	Wood chips	Cradle-to- gate	1 MW of H ₂	CML2001	GWP, AP, EP, HTP, ADP	Gabi	Literatures, AspenPlus simulation	No/No	[228]

Gasification	Steam	Poplar wood chips	Cradle-to-gate	1 Nm ³ of hydrogen	CML2001	CED, GWP, ODP, POE, LC, AP, EP	SimaPro	Ecoinvent, literatures,	No/No	[229]
Gasification	Hydrothermal	Crude glycerol	Cradle-to-gate	1 kg of H ₂ produced	CML 2000	ADP, CED, GWP, ODP, POE, AP, EP	SimaPro	Ecoinvent, literatures, AspenPlus simulation	No/No	[230]
Gasification	Steam	Grape pruning waste	Cradle-to-gate	1 kg of H ₂ produced	IPCC2013 for GWP, USEtox for Etox and CML2001 for the rest	ADP, AP, EP GWP, ODP, POE, LC, Etox	SimaPro	Ecoinvent, literatures, questionnaire, Aspen and PestLCI simulation	No/No	[231]
Gasification	Steam/low-pressure	Short-rotation poplar	Cradle-to-gate	1 kg of H ₂ produced	IPCC2013 for GWP, VDI for CEDnr and	AP, EP, GWP, ODP, POE, LC, CEDnr	SimaPro	Ecoinvent, literatures,	No/No	[232]

	indirect				CML2001 for the			Aspen		
	gasifier				rest			simulation		
Gasification	-	Waste wood	Cradle-to- gate	-	Inventory analysis	GHG	-	literature	No/No	[233]
Gasification	Air	Pinus patula	Cradle-to- gate	1 MJ of H ₂ production	ReCiPe Midpoint method	CC, ODP, TA, PM, FE, ME, POF, HTP, TE, FWAE, MAE, WD, NRE	SimaPro	Ecoinvent, literatures, Aspen simulation	No/No	[234]
Gasification	Steam- oxygen IBFB	Agro-industrial residue	Cradle-to- gate	1 MJ of H ₂ production	CML2011	GWP, AP, EP, POF, CEDnr	SimaPro	literatures, simulation	Yes/No	[235]
Gasification	Air/FB or Air/EF	Canadian pine wood	Cradle-to- gate	1 kg of H ₂ produced	-	GHG, NRE	REET	Literatures, Aspen and REET simulation	No/No	[236]

Gasification	Oxygen or hydrothermal	Microalgae	Cradle-to-gate	1 MJ of H ₂ production	-	Water footprint	-	Literatures	Yes/Yes	[237]
Gasification	Air and steam	Rice husk	Cradle-to-grave	200 kWh of electricity generation	CML2000 for GHG; Eco-indicator 99 for endpoint damage categories	GHG, endpoint damage categories: HH, EQ, RD	SimaPro	Ecoinvent, Aspen and Matlab simulation, literatures	No/No	[238]
Gasification	Steam	Corn stover	Cradle-to-gate	1 kg of H ₂ produced	ReCiPe 2016	Midpoint: GWP, ODP, IRP, HOFp, EOFp, HTPc, HTPnc, TE, WD, FWAE, MAE, FE, PM, LC, FFP, TA	SimaPro	Ecoinvent, GREET, literatures	No/No	[239]

						Endpoint: HH, EQ, RD				
Gasification	Steam	Corn stover	Cradle-to- gate	1 kg of H ₂ produced	CML2001	GWP, AP, EP, POF, HTP	GaBi	REET simulation, literatures	No/No	[240]
Gasification	Solar- powered hydrother mal	Wood sawdust	Cradle-to- gate	1 kg of H ₂ produced	CML2000 for midpoint categories; ReCiPe for endpoint categories; CED for energy	Midpoint: GWP, ADP, AP, EP, ODP, POF; Endpoint: HH, EQ, RD; CED	SimaPro	Ecoinvent, literatures	Yes/No	[241]
Gasification	hydrother mal	Corn stalks	Cradle-to- gate	1 kg of H ₂ produced	IPCC	GWP	-	Experiment, Aspen	No/No	[242]

								simulation,		
								literatures		
MEC system	pilot-scale	Urban	Cradle-to-	1 kg of H ₂	IMPACT 2002+	Midpoint: GWP,	SimaPro	Ecoinvent,	No/No	[243]
	continuou	wastewater	gate	produced		AA, NRE, ODP		literatures		
	s flow					Endpoint: CC, RD,				
						HH, EQ				
Fermentation	DF-MEC	Corn Stover	Cradle-to-	1 kg of H ₂	ReCiPe 2016	Midpoint: GWP,	SimaPro	Ecoinvent,	No/No	[239]
followed by			gate	produced		ODP, IRP, HOFp,		REET,		
MEC						EOFP, HTPc,		literatures		
						HTPnc, TE, WD,				
						FWAE, MAE, FE,				
						PM, LC, FFP, TA				
						Endpoint: HH, EQ,				
						RD				

*“Cradle-to-gate” in this table means the process starts from feedstock (may or may not include the collection and transportation) to hydrogen (may or may not include the pressing and transportation), but does not include the usage of hydrogen. “Cradle-to-grave” in this table means the “Cradle-to-gate” plus the hydrogen usage stage.

**Some abbreviations: GWP: global warming potential; GHG: greenhouse gas emissions; CED: cumulative fossil energy demand; CEDnr: cumulative non-renewable energy demand (fossil plus nuclear); NRE: non-renewable energy; FFP: fossil resource scarcity; AP: acidification potential; TA: terrestrial acidification; AA: aquatic acidification; EP: eutrophication potential; FE: freshwater eutrophication; ME: marine eutrophication; POF: photochemical oxidant formation; EOF: photochemical oxidant formation: ecosystem quality; HOF: photochemical oxidant formation: human health; HTP: human toxicity; HTPc: human toxicity potential: cancer; HTPnc: human toxicity potential: non-cancer; Etox: Eco-toxicity; FWAE: Fresh water aquatic ecotoxicity; MAE: Marine aquatic ecotoxicity; TE: Terrestrial ecotoxicity; PM: particle matter formation; IRP: ionizing radiation; LC: land use competition; ODP: ozone layer depletion; ADP: abiotic depletion; WD: water depletion; HH: human health; EQ: ecosystem quality; RD: resource depletion; CC: climate change. SDPF: Sequential dark and photo fermentation; DF: dark fermentation; DG: Downdraft Gasifier; CFBG: Circulating Fluidized Bed Gasifier; DFBG: dual fluidized-bed gasifier; IBFB: Indirectly heated Bubbling Fluidized Bed gasifier; FB: fluidized bed gasifier; EF: entrained flow gasifier. LCIA: life cycle impact assessment; CLCD: Chinese life cycle database; GREET: The Greenhouse gases, Regulated Emissions, and Energy use in Transportation model.

3.2 Bibliographical statistics of the selected LCA studies

The reviewed articles are chosen based on the searched results from “Scopus database” with the keywords of “life cycle”, “hydrogen” and the corresponding technology, and with time limited from 2009 until July 2019. The initial searched results of 122 papers (research/review/conference papers and book chapters) were went through carefully to find the most relevant studies focusing on using waste to produce hydrogen with a life cycle environmental analysis. Finally, only 30 papers were identified to be the relevant studies as shown in Table 6, which included five papers about fermentation, 23 papers about gasification and two papers about MEC (Fig. 10a).

The first stage of a LCA study is the goal and scope definition. In general, all the reviewed studies had a clear functional unit and system boundaries. The most commonly used functional unit was a certain amount of hydrogen produced, which can be evaluated by weight, energy or volume. However, in some cases, a quantified electricity generated from hydrogen or the road distance of hydrogen-powered facility or the amount of waste treated, can also be used as functional unit. In more than 85% of the studies, the system boundaries were limited to either the hydrogen produced at the gate or hydrogen ready for use, so-called cradle-to-gate analysis; while only a few studies included the hydrogen usage phase into the whole life cycle, so-called cradle-to-grave analysis (Fig. 10d). The data used in a LCA study consists of the life cycle inventory and the data quality is important for the reliability of the final result. As can be seen from Table 6, the data used for most of the reviewed studies came from literatures, model simulation and different database, such as Ecoinvent, GREET, etc.; while only a few studies used the first-hand experimental data from the same authors. In the reviewed studies, four of them focused only on life cycle inventory analysis and three of them did not mention the used life cycle

impact assessment (LCIA) methodology; while for the rest of studies, CML methodology was the most used LCIA methodology, followed by IPCC and ReCiPe method (Fig. 10e). At the impact assessment stage, two different LCA modelling can be found: midpoint and endpoint modelling [244]. The midpoint assessment is in the early stage of the cause-effect chain focusing on each individual problem; while endpoint assessment is at the end of cause-effect chain focusing at damage levels and aggregating different midpoint problems together. Both modelling were found among the reviewed studies, with more midpoint assessment compared to endpoint. Regarding the different environmental categories, as shown in Fig. 10f, the top five most discussed categories were identified to be global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), photochemical oxidant formation (POF) and ozone layer depletion (ODP). Moreover, around half of the LCA studies were performed with SimaPro, which was identified to be the most popular software, followed by Gabi (Fig. 10b). It must be mentioned that sensitivity and/or uncertainty analysis is recommended in the ISO14040 and can increase the robustness of the LCA results. However, only five out of the thirty reviewed papers performed sensitivity analysis (scenario analysis was used), and only one did the uncertainty analysis (Monte Carlo was used), which clearly indicated that the robustness of the majority hydrogen production LCA studies from waste through fermentation, gasification and MEC, was poorly evaluated and the quality needs to be further improved.

Fig. 10. The statistics of papers about LCA studies of biohydrogen production from waste and wastewater via different technologies (fermentation, gasification and MEC) that were published since 2009 based on the “Scopus database” (access date: 31 July 2019): a) the number of published papers; b) the adopted LCA software; c) the status of performing sensitivity/uncertainty analysis; d) the system boundaries definition information; e) the top five used LCIA methodologies; f) the top five discussed impact categories: GWP: global warming potential; AP: acidification potential; EP: eutrophication potential; POF: photochemical oxidant formation; ODP: ozone layer depletion.

3.3 Detailed research status progress

As shown in Table 6, the typical feedstocks used in LCA studies of fermentation were mainly agricultural waste and microalgae, while the waste used in gasification were normally agricultural and forestry wastes. Municipal solid waste, waste tyres, microalgae and industrial crude glycerol can also be found in gasification LCA studies for hydrogen production. Whereas the LCA studies about hydrogen generation via MEC technology are really limited and the detailed one used urban wastewater as feedstock. As mentioned above, GHG is the most common impact category that is discussed in all the studies, thus an overall overview of the GHG emissions of different technologies were compared. The results (Fig. 11) showed that a generally better performance with regard to GHG emissions can be found in waste gasification, compared to not only fermentation and MEC, but also the conventional hydrogen producing technologies, i.e. natural gas steam reforming, coal gasification and water electrolysis via grid electricity. The detailed review and discussion of each individual technology are as follows.

Fig. 11. The GHG emissions (kg CO₂-eq/kg H₂) range distribution of the reviewed three hydrogen production technologies (fermentation [217, 218, 220], gasification [19, 220, 224, 227, 229, 232-235, 239, 241] and MEC [243]) and the three conventional technologies (electricity water electrolysis [224, 245], coal gasification [224, 239, 246] and steam methane reforming [224, 227, 239, 247]).

The LCA results of a consequential dark and photo fermentation to produce hydrogen from potato steam peels showed that both the GHG emissions and the overall impacts of the proposed fermentation technology performed worse compared to the conventional natural gas or biogas reforming [216]. However, in another study performed by Djomo and Blumberga [217], three different wastes, including wheat straw (WS), sweet sorghum stalk (SSS) and steam potato peels (SPP), were used to produce hydrogen through consequential dark and photo fermentation. The authors calculated the GHG emissions

without considering the byproduct (proteinaceous animal feed) as 5.60, 5.32 and 5.18 kg CO₂-eq/kg H₂ for WS, SSS and SPP, respectively, and all of them were lower compared to steam methane reforming process. The main difference of the two studies causing the opposite results was the hydrogen production efficiency. For example, the hydrogen yield of SPP used in the latter study was three times higher than the one used in the former study. The comparison of the two studies also indicated the importance of choosing the appropriate data when performing a LCA study. Microalgae was also used for hydrogen production through dark fermentation, and 5-6 kg CO₂/MJ H₂ was reported, among which the cultivation of the microalgae contributed more than half of the emissions, while the emissions during the fermentation process varied from 150 to 370 g CO₂/MJ H₂ depending on different optimized parameters [218]. The similar result was also reported by Pacheco et al. [220] about treating microalgae to produce pigment and hydrogen. However, the author also emphasized that different allocation methods could result in different LCA results. On the contrary, when the microalgae was cultivated with artificial light, the high energy consumption resulted in high CO₂ emissions, i.e. 670 kg CO₂/MJ H₂ with more than 98% from the cultivation stages [219]. Except for the aforementioned studies focusing hydrogen production, other studies can also be found when hydrogen generation coupled with other technologies, such as anaerobic digestion, enzyme production, etc. [248, 249], which are not discussed in this paper due to the limited scope.

Unlike fermentation technology, almost all the LCA studies of hydrogen production from waste materials (mainly agricultural and forestry waste) through gasification had a better environmental profile compared to the conventional technologies [224, 228, 231, 240]. Wulf and Kaltschmitt [224] compared different hydrogen production pathways: green electricity electrolysis, conventional electricity electrolysis, methane reforming,

coal gasification, and wood chips gasification. The GHG emission results based on IPCC 2007 assessment methodology highlighted the environmental benefits of pathways of wood gasification and green electricity electrolysis. The similar result was also reported by Siddiqui and Dincer [240] that corn stover gasification (4.4 kg CO₂-eq/kg H₂) had the lowest GHG emissions compared to ethanol reforming (12.2 kg CO₂-eq/kg H₂), steam methane reforming (13.8 kg CO₂-eq/kg H₂), methanol reforming (17.9 kg CO₂-eq/kg H₂), coal gasification (23.7 kg CO₂-eq/kg H₂) and water electrolysis (28.6 kg CO₂-eq/kg H₂). Moreover, the crude glycerol was used to produce hydrogen through hydrothermal gasification, and the results showed GHG emissions of 3.77 kg CO₂-eq/kg H₂, which was much better compared to coal gasification and natural gas reforming [230]. In another study of solar-powered hydrothermal gasification treating wood sawdust to produce hydrogen, the GHG emission of 4.41 kg CO₂-eq/kg H₂ was observed, which was comparable to the hydrogen production from solar-powered water splitting method. Moreno and Dufour [226] investigated the GHG emissions of four different lignocellulosic wastes (i.e. pine, vine pruning, eucalyptus, and almond pruning). The results showed that eucalyptus was the feedstock with the lowest GHG emissions; while the emissions of all the four types of feedstocks were lower compared to the conventional technologies. In a cradle-to-grave LCA study, i.e. the hydrogen usage was considered, switchgrass was used to produce hydrogen through gasification, then the hydrogen was transported to exchange station and used as energy source for fuel cell scooter [222]. The authors concluded that the scooter powered by hydrogen from switchgrass gasification had much lower GHG emissions than the one powered by hydrogen from natural gas reforming.

On the other hand, the environmental profile of different gasification technologies were also compared by different researchers. Kalinci et al. [19] compared hydrogen production from pine wood through two different types of gasifier (Downdraft Gasifier (DG); Circulating Fluidized Bed Gasifier (CFBG)), and included the pine wood chopping, transportation, gasification operation, hydrogen pressing and transportation into the study. The authors concluded that the GHG emissions were 6.27 and 17.13 g CO₂-eq/MJ H₂ for DG and CFBG, respectively, which were comparable or even better than natural gas steam reforming and biomass based electrolysis. It was also found that the hydrogen pressing process contributed the most to the GHG emission in both types, and followed by hydrogen transportation, indicating the importance of taking the hydrogen usage into consideration during LCA analysis. Different gasification technologies were used to produce a fixed hydrogen concentration syngas by Khoo [221], including pyrolysis-gasification of MSW, combined pyrolysis, gasification and oxidation of MSW, thermal cracking gasification of granulated MSW, steam gasification of wood, gasification of refuse-derived fuel, circulating fluidized bed gasification of organic wastes and the gasification of waste tyres. The normalized LCA results showed that steam gasification of wood chips and pyrolysis-gasification of MSW had the lowest environmental impacts.

CO₂ capture was also developed in these years coupled with gasification to further reduce GHG emissions and even achieve negative emissions [232, 236]. However, it was reported by Susmozas et al. [232] that only the impact of GWP was better when CO₂ capture was implemented, while all the other impacts, such as ozone layer depletion, acidification potential, eutrophication potential, etc., were worse compared to the scenario without CO₂ capture, which indicated that optimization of the CO₂ capture technology is needed in order to achieve an overall improved environmental performance.

Furthermore, it must be mentioned that life cycle sustainability assessment (LCSA) that includes environmental, social and economic aspects were also investigated in comparison of different hydrogen producing methods [250]. The results highlighted the environmental benefits from biomass gasification compared to coal gasification, methane steam reforming and wind turbine electrolysis. However, only global warming potential and acidification potential were taken into consideration. A similar LCSA study were also performed by Valente et al. [251] to compare hydrogen production from biomass gasification and natural gas steam reforming, in which global warming potential and acidification potential (environmental pillar), levelised cost of hydrogen (economic pillar), and child labour, gender wage gap and health expenditure (social pillar) were taken into consideration. The authors suggested that even with environmental benefits, hydrogen from biomass gasification cannot yet be thoroughly considered as sustainable due to the poor performance on economic and social aspects.

In general, the LCA studies of MEC technology are few, and only three studies are found to be related to hydrogen generation from waste [239, 243, 252]. Only one of them gave the detailed description of each LCA stages that met the requirement of a high-quality LCA study. This study was done by Chen et al. [243] who investigated the environmental impacts of hydrogen production from urban wastewater, and the authors concluded that the current MEC technology needs to be further improved considering the relatively high GWP compared to conventional hydrogen production methods (Fig. 11). The results also showed that the emissions from the construction of the MEC system are the greatest contributor compared to operational emissions. The overall environmental impacts of the MEC systems increased with the increase of the applied external voltage, while decreased with the increase of the recovered hydrogen production and the

electricity transformation efficiency. The environmental impacts of MEC system producing/recovering chemicals other than hydrogen were reported, such as methanol [253], hydrogen peroxide [254, 255], ammonium [256], etc., and demonstrated the environmental benefits compared to the conventional synthesis method. However, this was not discussed in this paper considering they were out of scope of the current study.

4 Comparison, challenges and future perspectives

As discussed above, three main technologies, i.e. biological fermentation, thermochemical gasification and MEC system, have been proposed and investigated intensively to produce hydrogen from organic waste and wastewaters in the past ten years. However, each technology has its own advantages and disadvantages, as shown in Table 7. Facing the different waste feedstocks, gasification shows its advantage, because it can handle almost all the waste, except for the low-strength wastewater. For example, the hydrothermal gasification is competent for the wastes with high moisture contents (e.g. food waste, sludge and manure) [122]. Other low-water content solid wastes like agricultural and horticultural wastes can be also utilized for hydrogen production with other gasification technologies. It must be mentioned that plastic waste, which cannot be degraded through fermentation and MEC technology, can be easily treated through the two-stage pyrolysis and gasification system with high hydrogen production [128]. Moreover, the waste gasification also shows a low GHG emissions profile compared to other technologies based on the LCA results. On the other hand, dark fermentation can also accept a variety of waste materials, including different wastewater, food waste, MSW, etc., and a high hydrogen production rate is usually observed. Furthermore, the simple reactor configuration of the dark fermentation technology is also one of its important merits. Whereas the most obvious advantage of photo fermentation and MEC technology

is that both can achieve a high hydrogen yield and high COD/BOD removal rate, thus consequently result in high quality of the effluent [257].

However, even though a high hydrogen production rate can be observed for dark fermentation, the hydrogen yield is relatively low due to the high VFA production, thereafter results in high BOD levels in the effluent [257]. Another weakness of dark fermentation is that pretreatment is usually needed for the used mixed consortium in order to inhibit the methanogens, otherwise a potential oxidization of the produced hydrogen could happen to decrease the hydrogen concentration and yield [39]. When lignocellulosic waste materials are used as feedstock for dark fermentation, pretreatment should be performed to deconstruct the complex polymers. The same pretreatment also applies to MEC system when treating lignocellulose. Moreover, MEC system prefers hydrogen production recovery from different wastewater, instead of complex waste, such as food waste or municipal solid waste. In order to achieve a high hydrogen production rate, catalyst is usually coated on the cathode, which increases the overall cost and complexity of the MEC reactor. Regarding gasification, the main concern is the high temperature and sometimes high pressure working condition, which need special reactor building materials and configuration. Catalyst is also added in the gasification process to generate a high hydrogen content and yield. Furthermore, due to the complex syngas composition, the needed syngas reforming and further purification process could be regarded as another disadvantage of gasification.

According to the above discussed advantages and disadvantage, the technology development status, i.e. maturity, of each technology is also different. Even though no commercial scale plant has been reported based on the three technologies, the most mature one should be identified as gasification, followed by fermentation, while the MEC

system was the least mature technology. In April 2019, the construction of the first commercial scale waste-to-hydrogen gasification plant was announced in UK, targeting at treating 25 tonnes waste plastic and tyres per day to produce high quality hydrogen, which demonstrated the high maturity of gasification technology. Actually, a pilot scale plant treating five tonnes of municipal solid waste through plasma gasification to produce high purity hydrogen was also reported before in Cheongsong, South Korea. Meanwhile, a lot of small scale gasification treating different types of waste are also under development. As for fermentation technology, several pilot scale demonstrations have been reported. For example, a sequential dark (3 m^3) and photo (8 m^3) fermentation reactor was used to produce hydrogen with a production rate of around $60\text{ m}^3\text{ H}_2$ per day from corn stover in a local farm in Xu Chang, Henan Province, China; while a dark fermentation reactor with the similar production capacity treating food waste at the Indian Institute of Chemical Technology in Hyderabad was also reported. However, the practical application of MEC system is really limited and most of the reports were at laboratory scale focusing on optimization of different operational parameters and different trials of scaling up. The main bottleneck limiting the scale up of fermentation technologies are identified as the low stability of reactor performance and low hydrogen yield of dark fermentation [258], and also the low light conversion efficiency of photo fermentation process [97]. While a lot of issues exist and need to be solved before any further scale up of MEC technology, such as the low hydrogen production rate, the costly catalyst and membranes, the different performance of electrode materials, the unstable hydrogen production after long-term operation, etc. [259].

To overcome the aforementioned drawbacks, a lot of studies are needed. First of all, investigation of integrating dark fermentation with other technologies should be

performed, and the followed technology could be either MEC or anaerobic digestion or photo fermentation. Even though several similar researches have been reported [54, 200, 260], more studies are needed focusing on optimization of the operational parameters and comparison of different follow-up technologies. Moreover, to improve the overall energy efficiency of photo fermentation process, the optimization of light utilization needs further investigation. Thirdly, genetic engineering is more and more popular in these years and applied into different areas, thus investigation is expected to gene-modify microorganisms with special function to overcome the current limitation, such as low hydrogen yield and rate. Fourthly, catalyst is used to improve the hydrogen production and yield in both gasification and MEC system. The catalyst with outstanding activity is usually expensive with a short life span [157]. Therefore, the development on cheap and effective catalysts should be considered in the future. Furthermore, considering the rapidly developed micro biotechnology in these years, especially the dramatically reduced cost for high-throughput sequencing technology, more and more fundamental research is needed to decipher the microbial community and elucidate the working mechanisms of the biological process. Lastly, based on the reviewed LCA papers, more LCA case studies with high quality are needed in the future to evaluate the sustainability of the proposed technologies.

Table 7. An overall comparison of the three technologies

Technology	Advantages	Disadvantages and challenges	Future perspective
Fermentation	DF A wide variety of different waste; High hydrogen production rate; Simple reactor configuration.	A low hydrogen yield; The produced hydrogen might be oxidized by methanogens and/or homoacetogens; High BOD level in the effluent; Lignocellulose needs pretreatment; Inoculated consortium needs pretreatment.	Coupled with other technologies, e.g. AD, MEC, PF; Genetic engineering application; More high-quality LCA studies are needed.
	PF High hydrogen yield and COD removal rate.	Favourable to VFAs-rich wastewater and difficult to other wastes; Low hydrogen production rate; Light is needed but with low conversion efficiency and complex design.	Optimization of the light efficiency; Genetic engineering application; More high-quality LCA studies are needed.

Gasification	<p>Almost all the wastes, except for wastewater, particularly for plastic waste;</p> <p>Low GHG emissions.</p>	<p>Safety concern due to high temperature and sometimes high pressure;</p> <p>Catalyst is usually needed;</p> <p>Different compounds of the syngas.</p>	<p>Optimize the catalyst efficiency;</p> <p>Reduce the energy and material loss;</p> <p>Scale-up needs further to be tested;</p> <p>CO₂ capture strategy application;</p> <p>More high-quality LCA studies are needed.</p>
MEC system	<p>High hydrogen yield and COD removal rate;</p> <p>Works efficiently at room temperature, particularly in tropical regions.</p>	<p>Normally limited to wastewater and other waste needs pretreatment;</p> <p>The produced hydrogen might be oxidized by methanogens and/or homoacetogens;</p> <p>External voltage is needed.</p> <p>Low hydrogen production rate;</p> <p>Catalyst is needed for the electrode;</p>	<p>Research of scale-up should be conducted;</p> <p>The microorganisms and the electrons transfer mechanism need further study;</p> <p>More research about developing cheap and effective catalyst;</p> <p>CO₂ capture strategy application.</p> <p>More high-quality LCA studies are needed;</p>

*Some abbreviations: DF: dark fermentation; PF: photo fermentation; AD: anaerobic digestion; MEC: microbial electrolysis cell; LCA: life cycle assessment; BOD: biochemical oxygen demand; COD: chemical oxygen demand.

5 Conclusions

Through a holistic review, the current study demonstrated that biohydrogen is one of the future clean and green energy source that has the potential possibility to share a part of the fossil fuel consumption. The simultaneous disposal of waste and production of hydrogen can be achieved through different technologies, i.e. biological fermentation, thermochemical gasification and microbial electrolysis cell. Specifically, gasification is found to be the most studied technology, followed by dark fermentation and photo fermentation, and microbial electrolysis cell technology is the least investigated. A variety of waste materials, including different types of wastewater, agricultural and forestry residuals, sewage sludge, food waste, municipal solid waste, etc., have been used as feedstocks to produce hydrogen. Different types of wastewater were the most studied wastes in fermentation and microbial electrolysis cell, while wood waste was the most investigated one in gasification. Meanwhile, agricultural lignocellulosic residual and municipal solid waste was also widely used in fermentation and gasification studies, respectively. Whereas the hydrogen production rate and yield, varied significantly from waste to waste, and the carbohydrate content, instead of lipid and protein, determined the hydrogen production efficiency. However, the hydrogen efficiency was also influenced by a lot of parameters in each specific technology process. An optimization of the operational parameters can maximize the hydrogen production and minimize the waste quantity. Moreover, it is also found that dark fermentation had a high hydrogen production rate, but a low production yield. On the contrary, photo fermentation and microbial electrolysis cell technology had a relatively slow production rate, but a high production yield. Thus an integration of different technologies, instead of sticking on one single technology, should be considered. On the other hand, the results also showed that

most of the current the life cycle assessment studies of different waste-to-hydrogen production technologies had an overall low quality, especially the robustness of sensitivity and uncertainty analysis, indicating that more high-quality life cycle assessment studies should be performed in the future.

Acknowledgements

This work was supported by the National Research Foundation, Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) Programme.

References

- [1] Enerdata. Global Energy Statistical Yearbook, <https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html>. 2019.
- [2] EIA US. International Energy Outlook 2017. 2017.
- [3] Xu L, Chen N, Chen Z. Will China make a difference in its carbon intensity reduction targets by 2020 and 2030? Appl Energy. 2017;203:874-82.
- [4] Kaza S, Yao L, Bhada-Tata P, Van Woerden F. What a waste 2.0: a global snapshot of solid waste management to 2050: World Bank Publications; 2018.
- [5] Tokimatsu K, Konishi S, Ishihara K, Tezuka T, Yasuoka R, Nishio M. Role of innovative technologies under the global zero emissions scenarios. Appl Energy. 2016;162:1483-93.
- [6] Beyene HD, Werkneh AA, Ambaye TG. Current updates on waste to energy (WtE) technologies: a review. Renew Energy Focus. 2018;24:1-11.

- [7] Srirangan K, Akawi L, Moo-Young M, Chou CP. Towards sustainable production of clean energy carriers from biomass resources. *Appl Energy*. 2012;100:172-86.
- [8] Dutta S. A review on production, storage of hydrogen and its utilization as an energy resource. *J Ind Eng Chem*. 2014;20:1148-56.
- [9] Yin Y, Wang J. Biohydrogen production using waste activated sludge disintegrated by gamma irradiation. *Appl Energy*. 2015;155:434-9.
- [10] Dincer I. Green methods for hydrogen production. *Int J Hydrogen Energy*. 2012;37:1954-71.
- [11] Zakkour P, Cook G. CCS Roadmap for Industry: High-purity CO₂ sources. Carbon Counts Company Ltd: UK. 2010.
- [12] IEA. Technology Roadmap-Hydrogen and Fuel Cells. 2015.
- [13] Hanley ES, Deane JP, Gallachóir BPÓ. The role of hydrogen in low carbon energy futures—A review of existing perspectives. *Renew Sust Energy Rev*. 2018;82:3027-45.
- [14] Acar C, Dincer I. Comparative assessment of hydrogen production methods from renewable and non-renewable sources. *Int J Hydrogen Energy*. 2014;39:1-12.
- [15] Zhang Y, Angelidaki I. Microbial electrolysis cells turning to be versatile technology: Recent advances and future challenges. *Water Res*. 2014;56:11-25.
- [16] Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. *Renew Sust Energy Rev*. 2017;67:597-611.
- [17] Dincer I, Acar C. Review and evaluation of hydrogen production methods for better sustainability. *Int J Hydrogen Energy*. 2015;40:11094-111.
- [18] Ahamed A, Yin K, Ng BJH, Ren F, Chang VWC, Wang JY. Life cycle assessment of the present and proposed food waste management technologies from environmental and economic impact perspectives. *J Cleaner Prod*. 2016;131:607-14.

- [19] Kalinci Y, Hepbasli A, Dincer I. Life cycle assessment of hydrogen production from biomass gasification systems. *Int J Hydrogen Energy*. 2012;37:14026-39.
- [20] Valente A, Iribarren D, Dufour J. Life cycle assessment of hydrogen energy systems: a review of methodological choices. *Int J Life Cycle Assess*. 2017;22:346-63.
- [21] Elbeshbishy E, Dhar BR, Nakhla G, Lee H-S. A critical review on inhibition of dark biohydrogen fermentation. *Renew Sust Energy Rev*. 2017;79:656-68.
- [22] Wong YM, Wu TY, Juan JC. A review of sustainable hydrogen production using seed sludge via dark fermentation. *Renew Sust Energy Rev*. 2014;34:471-82.
- [23] Rodriguez Correa C, Kruse A. Supercritical water gasification of biomass for hydrogen production – Review. *J Supercrit Fluids*. 2018;133:573-90.
- [24] Kadier A, Simayi Y, Abdeshahian P, Azman NF, Chandrasekhar K, Kalil MS. A comprehensive review of microbial electrolysis cells (MEC) reactor designs and configurations for sustainable hydrogen gas production. *Alex Eng J*. 2016;55:427-43.
- [25] Kundu A, Sahu JN, Redzwan G, Hashim MA. An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell. *Int J Hydrogen Energy*. 2013;38:1745-57.
- [26] Guo XM, Trably E, Latrille E, Carrère H, Steyer J-P. Hydrogen production from agricultural waste by dark fermentation: A review. *Int J Hydrogen Energy*. 2010;35:10660-73.
- [27] Baykara SZ. Hydrogen: A brief overview on its sources, production and environmental impact. *Int J Hydrogen Energy*. 2018;43:10605-14.
- [28] Watson J, Zhang Y, Si B, Chen W-T, de Souza R. Gasification of biowaste: A critical review and outlooks. *Renew Sust Energy Rev*. 2018;83:1-17.

- [29] Lin C-Y, Nguyen TM-L, Chu C-Y, Leu H-J, Lay C-H. Fermentative biohydrogen production and its byproducts: A mini review of current technology developments. *Renew Sust Energy Rev.* 2018;82:4215-20.
- [30] Show K-Y, Lee D-J, Chang J-S. Bioreactor and process design for biohydrogen production. *Bioresour Technol.* 2011;102:8524-33.
- [31] Ghimire A, Frunzo L, Pirozzi F, Trably E, Escudie R, Lens PNL, et al. A review on dark fermentative biohydrogen production from organic biomass: Process parameters and use of by-products. *Appl Energy.* 2015;144:73-95.
- [32] Hallenbeck PC. Fermentative hydrogen production: Principles, progress, and prognosis. *Int J Hydrogen Energy.* 2009;34:7379-89.
- [33] Ortigueira J, Alves L, Gouveia L, Moura P. Third generation biohydrogen production by *Clostridium butyricum* and adapted mixed cultures from *Scenedesmus obliquus* microalga biomass. *Fuel.* 2015;153:128-34.
- [34] Wang J, Yin Y. Progress in microbiology for fermentative hydrogen production from organic wastes. *Crit Rev Environ Sci Technol.* 2019;49:825-65.
- [35] Alibardi L, Cossu R. Effects of carbohydrate, protein and lipid content of organic waste on hydrogen production and fermentation products. *Waste Manage.* 2016;47:69-77.
- [36] Xia A, Cheng J, Ding L, Lin R, Song W, Su H, et al. Substrate consumption and hydrogen production via co-fermentation of monomers derived from carbohydrates and proteins in biomass wastes. *Appl Energy.* 2015;139:9-16.
- [37] Guo P, Mochidzuki K, Cheng W, Zhou M, Gao H, Zheng D, et al. Effects of different pretreatment strategies on corn stalk acidogenic fermentation using a microbial consortium. *Bioresour Technol.* 2011;102:7526-31.

- [38] Eskicioglu C, Monlau F, Barakat A, Ferrer I, Kaparaju P, Trably E, et al. Assessment of hydrothermal pretreatment of various lignocellulosic biomass with CO₂ catalyst for enhanced methane and hydrogen production. *Water Res.* 2017;120:32-42.
- [39] Łukajtis R, Hołowacz I, Kucharska K, Glinka M, Rybarczyk P, Przyjazny A, et al. Hydrogen production from biomass using dark fermentation. *Renew Sust Energy Rev.* 2018;91:665-94.
- [40] Leñaño EP, Anceno AJ, Babel S. Ultrasonic pretreatment of palm oil mill effluent: Impact on biohydrogen production, bioelectricity generation, and underlying microbial communities. *Int J Hydrogen Energy.* 2012;37:12241-9.
- [41] Leñaño EP, Babel S. The influence of enzyme and surfactant on biohydrogen production and electricity generation using Palm Oil Mill Effluent. *J Cleaner Prod.* 2012;31:91-9.
- [42] Xing Y, Li Z, Fan Y, Hou H. Biohydrogen production from dairy manures with acidification pretreatment by anaerobic fermentation. *Environ Sci Pollut Res.* 2010;17:392-9.
- [43] Monlau F, Barakat A, Trably E, Dumas C, Steyer J-P, Carrère H. Lignocellulosic Materials Into Biohydrogen and Biomethane: Impact of Structural Features and Pretreatment. *Crit Rev Environ Sci Technol.* 2013;43:260-322.
- [44] Rai PK, Singh SP, Asthana RK, Singh S. Biohydrogen production from sugarcane bagasse by integrating dark- and photo-fermentation. *Bioresour Technol.* 2014;152:140-6.
- [45] Kongjan P, O-Thong S, Kotay M, Min B, Angelidaki I. Biohydrogen production from wheat straw hydrolysate by dark fermentation using extreme thermophilic mixed culture. *Biotechnol Bioeng.* 2010;105:899-908.

- [46] Cao G-L, Guo W-Q, Wang A-J, Zhao L, Xu C-J, Zhao Q-l, et al. Enhanced cellulosic hydrogen production from lime-treated cornstalk wastes using thermophilic anaerobic microflora. *Int J Hydrogen Energy*. 2012;37:13161-6.
- [47] Gonzales RR, Kim S-H. Dark fermentative hydrogen production following the sequential dilute acid pretreatment and enzymatic saccharification of rice husk. *Int J Hydrogen Energy*. 2017;42:27577-83.
- [48] Xia A, Cheng J, Ding L, Lin R, Song W, Zhou J, et al. Enhancement of energy production efficiency from mixed biomass of *Chlorella pyrenoidosa* and cassava starch through combined hydrogen fermentation and methanogenesis. *Appl Energy*. 2014;120:23-30.
- [49] Yang G, Wang J. Enhanced Hydrogen Production from Sewage Sludge by Co-fermentation with Forestry Wastes. *Energy Fuels*. 2017;31:9633-41.
- [50] Silva FMS, Mahler CF, Oliveira LB, Bassin JP. Hydrogen and methane production in a two-stage anaerobic digestion system by co-digestion of food waste, sewage sludge and glycerol. *Waste Manage*. 2018;76:339-49.
- [51] Laurinavichene T, Tekucheva D, Laurinavichius K, Tsygankov A. Utilization of distillery wastewater for hydrogen production in one-stage and two-stage processes involving photofermentation. *Enzyme Microb Technol*. 2018;110:1-7.
- [52] Sen B, Suttar RR. Mesophilic fermentative hydrogen production from sago starch-processing wastewater using enriched mixed cultures. *Int J Hydrogen Energy*. 2012;37:15588-97.
- [53] Intanoo P, Chaimongkol P, Chavadej S. Hydrogen and methane production from cassava wastewater using two-stage upflow anaerobic sludge blanket reactors (UASB)

with an emphasis on maximum hydrogen production. *Int J Hydrogen Energy*. 2016;41:6107-14.

[54] Cheng J, Lin R, Xia A, Liu Y, Zhou J, Cen K. Sequential Generation of Fermentative Hydrogen and Methane from Swine Manure with Physicochemical Characterization. *Energy Fuels*. 2014;28:563-70.

[55] Srivastava N, Srivastava M, Kushwaha D, Gupta VK, Manikanta A, Ramteke PW, et al. Efficient dark fermentative hydrogen production from enzyme hydrolyzed rice straw by *Clostridium pasteurianum* (MTCC116). *Bioresour Technol*. 2017;238:552-8.

[56] Han W, Ye M, Zhu AJ, Zhao HT, Li YF. Batch dark fermentation from enzymatic hydrolyzed food waste for hydrogen production. *Bioresour Technol*. 2015;191:24-9.

[57] Xiao L, Deng Z, Fung KY, Ng KM. Biohydrogen generation from anaerobic digestion of food waste. *Int J Hydrogen Energy*. 2013;38:13907-13.

[58] Kim D-H, Wu J, Jeong K-W, Kim M-S, Shin H-S. Natural inducement of hydrogen from food waste by temperature control. *Int J Hydrogen Energy*. 2011;36:10666-73.

[59] Massanet-Nicolau J, Guwy A, Dinsdale R, Premier G, Esteves S. Production of hydrogen from sewage biosolids in a continuously fed bioreactor: Effect of hydraulic retention time and sparging. *Int J Hydrogen Energy*. 2010;35:469-78.

[60] Romero Aguilar MA, Fdez-Güelfo LA, Álvarez-Gallego CJ, Romero García LI. Effect of HRT on hydrogen production and organic matter solubilization in acidogenic anaerobic digestion of OFMSW. *Chem Eng J*. 2013;219:443-9.

[61] Bru K, Blazy V, Joulain C, Trably E, Latrille E, Quéméneur M, et al. Innovative CO₂ pretreatment for enhancing biohydrogen production from the organic fraction of municipal solid waste (OFMSW). *Int J Hydrogen Energy*. 2012;37:14062-71.

- [62] Tenca A, Schievano A, Perazzolo F, Adani F, Oberti R. Biohydrogen from thermophilic co-fermentation of swine manure with fruit and vegetable waste: Maximizing stable production without pH control. *Bioresour Technol.* 2011;102:8582-8.
- [63] Silva FMS, Oliveira LB, Mahler CF, Bassin JP. Hydrogen production through anaerobic co-digestion of food waste and crude glycerol at mesophilic conditions. *Int J Hydrogen Energy.* 2017;42:22720-9.
- [64] Cipolla A, Delbrassine F, Da Lage J-L, Feller G. Temperature adaptations in psychrophilic, mesophilic and thermophilic chloride-dependent alpha-amylases. *Biochimie.* 2012;94:1943-50.
- [65] Wang J, Wan W. Factors influencing fermentative hydrogen production: A review. *Int J Hydrogen Energy.* 2009;34:799-811.
- [66] Azbar N, Dokgöz FT, Keskin T, Eltem R, Korkmaz KS, Gezgin Y, et al. Comparative Evaluation of Bio-Hydrogen Production From Cheese Whey Wastewater Under Thermophilic and Mesophilic Anaerobic Conditions. *Int J Green Energy.* 2009;6:192-200.
- [67] Li C, Fang HHP. Fermentative Hydrogen Production From Wastewater and Solid Wastes by Mixed Cultures. *Crit Rev Environ Sci Technol.* 2007;37:1-39.
- [68] Chou C-H, Wang C-W, Huang C-C, Lay J-J. Pilot study of the influence of stirring and pH on anaerobes converting high-solid organic wastes to hydrogen. *Int J Hydrogen Energy.* 2008;33:1550-8.
- [69] Rajhi H, Puyol D, Martínez MC, Díaz EE, Sanz JL. Vacuum promotes metabolic shifts and increases biogenic hydrogen production in dark fermentation systems. *Front Environ Sci Eng.* 2016;10:513-21.

- [70] Veeravalli SS, Chaganti SR, Lalman JA, Heath DD. Fermentative H₂ production using a switchgrass steam exploded liquor fed to mixed anaerobic cultures: Effect of hydraulic retention time, linoleic acid and nitrogen sparging. *Int J Hydrogen Energy*. 2014;39:9994-10002.
- [71] Rosa PRF, Santos SC, Sakamoto IK, Varesche MBA, Silva EL. Hydrogen production from cheese whey with ethanol-type fermentation: Effect of hydraulic retention time on the microbial community composition. *Bioresour Technol*. 2014;161:10-9.
- [72] Singh L, Wahid ZA, Siddiqui MF, Ahmad A, Rahim MHA, Sakinah M. Biohydrogen production from palm oil mill effluent using immobilized *Clostridium butyricum* EB6 in polyethylene glycol. *Process Biochem*. 2013;48:294-8.
- [73] Pachapur VL, Sarma SJ, Brar SK, Bihan YL, Buelna G, Verma M. Hydrogen production from biodiesel industry waste by using a co-culture of *Enterobacter aerogenes* and *Clostridium butyricum*. *Biofuels*. 2017;8:651-62.
- [74] Phowan P, Reungsang A, Danvirutai P. Bio-hydrogen production from cassava pulp hydrolysate using co-culture of *Clostridium butyricum* and *Enterobacter aerogenes*. *Biotechnology*. 2010;9:348-54.
- [75] Wong YM, Juan JC, Ting A, Wu TY. High efficiency bio-hydrogen production from glucose revealed in an inoculum of heat-pretreated landfill leachate sludge. *Energy*. 2014;72:628-35.
- [76] Lee K-S, Tseng T-S, Liu Y-W, Hsiao Y-D. Enhancing the performance of dark fermentative hydrogen production using a reduced pressure fermentation strategy. *Int J Hydrogen Energy*. 2012;37:15556-62.

- [77] Yin Y, Wang J. Changes in microbial community during biohydrogen production using gamma irradiated sludge as inoculum. *Bioresour Technol.* 2016;200:217-22.
- [78] Chen C-C, Chuang Y-S, Lin C-Y, Lay C-H, Sen B. Thermophilic dark fermentation of untreated rice straw using mixed cultures for hydrogen production. *Int J Hydrogen Energy.* 2012;37:15540-6.
- [79] Koku H, Eroğlu İ, Gündüz U, Yücel M, Türker L. Aspects of the metabolism of hydrogen production by *Rhodobacter sphaeroides*. *Int J Hydrogen Energy.* 2002;27:1315-29.
- [80] Tao Y, He Y, Wu Y, Liu F, Li X, Zong W, et al. Characteristics of a new photosynthetic bacterial strain for hydrogen production and its application in wastewater treatment. *Int J Hydrogen Energy.* 2008;33:963-73.
- [81] Ghosh S, Dairkee UK, Chowdhury R, Bhattacharya P. Hydrogen from food processing wastes via photofermentation using Purple Non-sulfur Bacteria (PNSB) – A review. *Energy Convers Manage.* 2017;141:299-314.
- [82] Lu C, Zhang Z, Ge X, Wang Y, Zhou X, You X, et al. Bio-hydrogen production from apple waste by photosynthetic bacteria HAU-M1. *Int J Hydrogen Energy.* 2016;41:13399-407.
- [83] Jiang D, Ge X, Zhang T, Liu H, Zhang Q. Photo-fermentative hydrogen production from enzymatic hydrolysate of corn stalk pith with a photosynthetic consortium. *Int J Hydrogen Energy.* 2016;41:16778-85.
- [84] Androga DD, Özgür E, Eroglu I, Gündüz U, Yücel M. Significance of carbon to nitrogen ratio on the long-term stability of continuous photofermentative hydrogen production. *Int J Hydrogen Energy.* 2011;36:15583-94.

- [85] Seifert K, Waligorska M, Laniecki M. Hydrogen generation in photobiological process from dairy wastewater. *Int J Hydrogen Energy*. 2010;35:9624-9.
- [86] Singh R. Fermentative Biohydrogen Production Using Microbial Consortia. In: Gupta VK, Tuohy MG, editors. *Biofuel Technologies: Recent Developments*. Berlin, Heidelberg: Springer Berlin Heidelberg; 2013. p. 273-99.
- [87] Zhang Z, Wang Y, Hu J, Wu Q, Zhang Q. Influence of mixing method and hydraulic retention time on hydrogen production through photo-fermentation with mixed strains. *Int J Hydrogen Energy*. 2015;40:6521-9.
- [88] Ozmihci S, Kargi F. Bio-hydrogen production by photo-fermentation of dark fermentation effluent with intermittent feeding and effluent removal. *Int J Hydrogen Energy*. 2010;35:6674-80.
- [89] Zhang Q, Zhang Z, Wang Y, Lee D-J, Li G, Zhou X, et al. Sequential dark and photo fermentation hydrogen production from hydrolyzed corn stover: A pilot test using 11 m³ reactor. *Bioresour Technol*. 2018;253:382-6.
- [90] Adessi A, Torzillo G, Baccetti E, De Philippis R. Sustained outdoor H₂ production with *Rhodospseudomonas palustris* cultures in a 50L tubular photobioreactor. *Int J Hydrogen Energy*. 2012;37:8840-9.
- [91] Nakada E, Asada Y, Arai T, Miyake J. Light penetration into cell suspensions of photosynthetic bacteria and relation to hydrogen production. *J Ferment Bioeng*. 1995;80:53-7.
- [92] Tian X, Liao Q, Zhu X, Wang Y, Zhang P, Li J, et al. Characteristics of a biofilm photobioreactor as applied to photo-hydrogen production. *Bioresour Technol*. 2010;101:977-83.

- [93] Sagir E, Ozgur E, Gunduz U, Eroglu I, Yucel M. Single-stage photofermentative biohydrogen production from sugar beet molasses by different purple non-sulfur bacteria. *Bioprocess Biosystems Eng.* 2017;40:1589-601.
- [94] Seifert K, Waligorska M, Laniecki M. Brewery wastewaters in photobiological hydrogen generation in presence of *Rhodobacter sphaeroides* O.U. 001. *Int J Hydrogen Energy.* 2010;35:4085-91.
- [95] Zhang Q, Wang Y, Zhang Z, Lee D-J, Zhou X, Jing Y, et al. Photo-fermentative hydrogen production from crop residue: A mini review. *Bioresour Technol.* 2017;229:222-30.
- [96] Basak N, Jana AK, Das D, Saikia D. Photofermentative molecular biohydrogen production by purple-non-sulfur (PNS) bacteria in various modes: The present progress and future perspective. *Int J Hydrogen Energy.* 2014;39:6853-71.
- [97] Zhang Z, Zhou X, Hu J, Zhang T, Zhu S, Zhang Q. Photo-bioreactor structure and light-heat-mass transfer properties in photo-fermentative bio-hydrogen production system: A mini review. *Int J Hydrogen Energy.* 2017;42:12143-52.
- [98] Wang X, Fang Y, Wang Y, Hu J, Zhang A, Ma X, et al. Single-stage photo-fermentative hydrogen production from hydrolyzed straw biomass using *Rhodobacter sphaeroides*. *Int J Hydrogen Energy.* 2018;43:13810-20.
- [99] Keskin T, Hallenbeck PC. Hydrogen production from sugar industry wastes using single-stage photofermentation. *Bioresour Technol.* 2012;112:131-6.
- [100] Eroğlu E, Eroğlu İ, Gündüz U, Yücel M. Treatment of olive mill wastewater by different physicochemical methods and utilization of their liquid effluents for biological hydrogen production. *Biomass Bioenergy.* 2009;33:701-5.

- [101] Chen C-Y, Liu C-H, Lo Y-C, Chang J-S. Perspectives on cultivation strategies and photobioreactor designs for photo-fermentative hydrogen production. *Bioresour Technol.* 2011;102:8484-92.
- [102] Bianchi L, Mannelli F, Viti C, Adessi A, De Philippis R. Hydrogen-producing purple non-sulfur bacteria isolated from the trophic lake Averno (Naples, Italy). *Int J Hydrogen Energy.* 2010;35:12216-23.
- [103] Kawagoshi Y, Oki Y, Nakano I, Fujimoto A, Takahashi H. Biohydrogen production by isolated halotolerant photosynthetic bacteria using long-wavelength light-emitting diode (LW-LED). *Int J Hydrogen Energy.* 2010;35:13365-9.
- [104] Subudhi S, Mogal SK, Ram Kumar N, Nayak T, Lal B, Velankar H, et al. Photo fermentative hydrogen production by a new strain; *Rhodobacter sphaeroides* CNT 2A, isolated from pond sediment. *Int J Hydrogen Energy.* 2016;41:13979-85.
- [105] Liu B-F, Jin Y-R, Cui Q-F, Xie G-J, Wu Y-N, Ren N-Q. Photo-fermentation hydrogen production by *Rhodopseudomonas* sp. nov. strain A7 isolated from the sludge in a bioreactor. *Int J Hydrogen Energy.* 2015;40:8661-8.
- [106] Özgür E, Mars AE, Peksel B, Louwerse A, Yücel M, Gündüz U, et al. Biohydrogen production from beet molasses by sequential dark and photofermentation. *Int J Hydrogen Energy.* 2010;35:511-7.
- [107] Kars G, Gündüz U, Yücel M, Rakhely G, Kovacs KL, Eroğlu İ. Evaluation of hydrogen production by *Rhodobacter sphaeroides* O.U.001 and its hupSL deficient mutant using acetate and malate as carbon sources. *Int J Hydrogen Energy.* 2009;34:2184-90.

- [108] Wang X, Yang H, Ma C, Guo L. Enhanced photosynthetic hydrogen production performance of *Rhodobacter capsulatus* by deactivating CBB cycle and cytochrome c oxidase. *Int J Hydrogen Energy*. 2014;39:3176-84.
- [109] Zheng GH, Wang L, Kang ZH. Feasibility of biohydrogen production from tofu wastewater with glutamine auxotrophic mutant of *Rhodobacter sphaeroides*. *Renew Energy*. 2010;35:2910-3.
- [110] Adessi A, De Philippis R. Photobioreactor design and illumination systems for H₂ production with anoxygenic photosynthetic bacteria: A review. *Int J Hydrogen Energy*. 2014;39:3127-41.
- [111] Chen C-Y, Yeh K-L, Lo Y-C, Wang H-M, Chang J-S. Engineering strategies for the enhanced photo-H₂ production using effluents of dark fermentation processes as substrate. *Int J Hydrogen Energy*. 2010;35:13356-64.
- [112] Argun H, Kargi F. Bio-hydrogen production by different operational modes of dark and photo-fermentation: An overview. *Int J Hydrogen Energy*. 2011;36:7443-59.
- [113] Mohanakrishna G, Mohan SV. Multiple process integrations for broad perspective analysis of fermentative H₂ production from wastewater treatment: Technical and environmental considerations. *Appl Energy*. 2013;107:244-54.
- [114] Zong W, Yu R, Zhang P, Fan M, Zhou Z. Efficient hydrogen gas production from cassava and food waste by a two-step process of dark fermentation and photo-fermentation. *Biomass Bioenergy*. 2009;33:1458-63.
- [115] Yang H, Guo L, Liu F. Enhanced bio-hydrogen production from corncob by a two-step process: Dark- and photo-fermentation. *Bioresour Technol*. 2010;101:2049-52.

- [116] Argun H, Kargi F, Kapdan IK. Effects of the substrate and cell concentration on bio-hydrogen production from ground wheat by combined dark and photo-fermentation. *Int J Hydrogen Energy*. 2009;34:6181-8.
- [117] Argun H, Kargi F. Effects of light source, intensity and lighting regime on bio-hydrogen production from ground wheat starch by combined dark and photo-fermentations. *Int J Hydrogen Energy*. 2010;35:1604-12.
- [118] Chandra R, Venkata Mohan S. Enhanced bio-hydrogenesis by co-culturing photosynthetic bacteria with acidogenic process: Augmented dark-photo fermentative hybrid system to regulate volatile fatty acid inhibition. *Int J Hydrogen Energy*. 2014;39:7604-15.
- [119] Argun H, Kargi F. Bio-hydrogen production from ground wheat starch by continuous combined fermentation using annular-hybrid bioreactor. *Int J Hydrogen Energy*. 2010;35:6170-8.
- [120] Sagnak R, Kargi F. Hydrogen gas production from acid hydrolyzed wheat starch by combined dark and photo-fermentation with periodic feeding. *Int J Hydrogen Energy*. 2011;36:10683-9.
- [121] Abdoulmoumine N, Adhikari S, Kulkarni A, Chattanathan S. A review on biomass gasification syngas cleanup. *Appl Energy*. 2015;155:294-307.
- [122] Okolie JA, Rana R, Nanda S, Dalai AK, Kozinski JA. Supercritical water gasification of biomass: A state-of-the-art review of process parameters, reaction mechanisms and catalysis. *Sustainable Energy Fuels*. 2019;3:578-98.
- [123] Peterson AA, Vogel F, Lachance RP, Fröling M, Antal Jr MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environ Sci*. 2008;1:32-65.

- [124] Arena U. Process and technological aspects of municipal solid waste gasification. A review. *Waste Manage.* 2012;32:625-39.
- [125] Nipattummakul N, Ahmed II, Gupta AK, Kerdsuwan S. Hydrogen and syngas yield from residual branches of oil palm tree using steam gasification. *Int J Hydrogen Energy.* 2011;36:3835-43.
- [126] Burra KG, Gupta AK. Synergistic effects in steam gasification of combined biomass and plastic waste mixtures. *Appl Energy.* 2018;211:230-6.
- [127] Lemmens B, Elslander H, Vanderreydt I, Peys K, Diels L, Oosterlinck M, et al. Assessment of plasma gasification of high caloric waste streams. *Waste Manage.* 2007;27:1562-9.
- [128] Wu C, Williams PT. Pyrolysis-gasification of plastics, mixed plastics and real-world plastic waste with and without Ni-Mg-Al catalyst. *Fuel.* 2010;89:3022-32.
- [129] Nanda S, Isen J, Dalai AK, Kozinski JA. Gasification of fruit wastes and agro-food residues in supercritical water. *Energy Convers Manage.* 2016;110:296-306.
- [130] Acomb JC, Wu C, Williams PT. Control of steam input to the pyrolysis-gasification of waste plastics for improved production of hydrogen or carbon nanotubes. *Appl Catal, B.* 2014;147:571-84.
- [131] Chen G, Liu F, Guo X, Zhang Y, Yan B, Cheng Z, et al. Co-gasification of Acid Hydrolysis Residues and Sewage Sludge in a Downdraft Fixed Gasifier with CaO as an In-Bed Additive. *Energy Fuels.* 2018;32:5893-900.
- [132] Parthasarathy P, Narayanan KS. Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield - A review. *Renew Energy.* 2014;66:570-9.

- [133] Chang ACC, Chang HF, Lin FJ, Lin KH, Chen CH. Biomass gasification for hydrogen production. *Int J Hydrogen Energy*. 2011;36:14252-60.
- [134] De Lasa H, Salaices E, Mazumder J, Lucky R. Catalytic steam gasification of biomass: Catalysts, thermodynamics and kinetics. *Chem Rev*. 2011;111:5404-33.
- [135] Luo S, Xiao B, Guo X, Hu Z, Liu S, He M. Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: Influence of particle size on gasification performance. *Int J Hydrogen Energy*. 2009;34:1260-4.
- [136] Shie JL, Chen LX, Lin KL, Chang CY. Plasmatron gasification of biomass lignocellulosic waste materials derived from municipal solid waste. *Energy*. 2014;66:82-9.
- [137] Lv P, Xiong Z, Chang J, Wu C, Chen Y, Zhu J. An experimental study on biomass air–steam gasification in a fluidized bed. *Bioresour Technol*. 2004;95:95-101.
- [138] Favas J, Monteiro E, Rouboa A. Hydrogen production using plasma gasification with steam injection. *Int J Hydrogen Energy*. 2017;42:10997-1005.
- [139] Lee IG, Kim MS, Ihm SK. Gasification of glucose in supercritical water. *Ind Eng Chem Res*. 2002;41:1182-8.
- [140] Ghani WAWAK, Moghadam RA, Salleh MAM, Alias AB. Air gasification of agricultural waste in a fluidized bed gasifier: Hydrogen production performance. *Energies*. 2009;2:258-68.
- [141] He M, Hu Z, Xiao B, Li J, Guo X, Luo S, et al. Hydrogen-rich gas from catalytic steam gasification of municipal solid waste (MSW): Influence of catalyst and temperature on yield and product composition. *Int J Hydrogen Energy*. 2009;34:195-203.

- [142] Lu Y, Guo L, Zhang X, Ji C. Hydrogen production by supercritical water gasification of biomass: Explore the way to maximum hydrogen yield and high carbon gasification efficiency. *Int J Hydrogen Energy*. 2012;37:3177-85.
- [143] Guo Y, Wang S, Gong Y, Xu D, Tang X, Ma H. Partial oxidation of municipal sludge with activated carbon catalyst in supercritical water. *J Hazard Mater*. 2010;180:137-44.
- [144] He C, Chen CL, Giannis A, Yang Y, Wang JY. Hydrothermal gasification of sewage sludge and model compounds for renewable hydrogen production: A review. *Renew Sust Energy Rev*. 2014;39:1127-42.
- [145] Zhang Q, Dor L, Fenigshtein D, Yang W, Blasiak W. Gasification of municipal solid waste in the Plasma Gasification Melting process. *Appl Energy*. 2012;90:106-12.
- [146] Sheth PN, Babu B. Production of hydrogen energy through biomass (waste wood) gasification. *Int J Hydrogen Energy*. 2010;35:10803-10.
- [147] Arnold RA, Hill JM. Catalysts for gasification: a review. *Sustainable Energy Fuels*. 2019;3:656-72.
- [148] Lahaye L, Ehrburger P. Fundamental issues in control of carbon gasification reactivity: Springer Science & Business Media; 2012.
- [149] Lobo LS. Intrinsic kinetics in carbon gasification: Understanding linearity, “nanoworms” and alloy catalysts. *Appl Catal, B*. 2014;148-149:136-43.
- [150] Muangrat R, Onwudili JA, Williams PT. Influence of alkali catalysts on the production of hydrogen-rich gas from the hydrothermal gasification of food processing waste. *Appl Catal, B*. 2010;100:440-9.

- [151] Muangrat R, Onwudili JA, Williams PT. Alkali-promoted hydrothermal gasification of biomass food processing waste: A parametric study. *Int J Hydrogen Energy*. 2010;35:7405-15.
- [152] Minowa T, Zhen F, Ogi T. Cellulose decomposition in hot-compressed water with alkali or nickel catalyst. *J Supercrit Fluids*. 1998;13:253-9.
- [153] Güngören Madenoğlu T, Boukis N, Sağlam M, Yüksel M. Supercritical water gasification of real biomass feedstocks in continuous flow system. *Int J Hydrogen Energy*. 2011;36:14408-15.
- [154] Elbaba IF, Wu C, Williams PT. Hydrogen production from the pyrolysis-gasification of waste tyres with a nickel/cerium catalyst. *Int J Hydrogen Energy*. 2011;36:6628-37.
- [155] Li J, Yin Y, Zhang X, Liu J, Yan R. Hydrogen-rich gas production by steam gasification of palm oil wastes over supported tri-metallic catalyst. *Int J Hydrogen Energy*. 2009;34:9108-15.
- [156] Chun YN, Song HW, Kim SC, Lim MS. Hydrogen-rich gas production from biogas reforming using plasmatron. *Energy Fuels*. 2007;22:123-7.
- [157] Richardson Y, Blin J, Julbe A. A short overview on purification and conditioning of syngas produced by biomass gasification: Catalytic strategies, process intensification and new concepts. *Prog Energy Combust Sci*. 2012;38:765-81.
- [158] Voldsund M, Jordal K, Anantharaman R. Hydrogen production with CO₂ capture. *Int J Hydrogen Energy*. 2016;41:4969-92.
- [159] Mendes D, Mendes A, Madeira L, Iulianelli A, Sousa J, Basile A. The water - gas shift reaction: from conventional catalytic systems to Pd - based membrane reactors—a review. *Asia-Pac J Chem Eng*. 2010;5:111-37.

- [160] Raggio G, Pettinau A, Orsini A, Fadda M, Cocco D, Deiana P, et al. Coal gasification pilot plant for hydrogen production. Part B: syngas conversion and hydrogen separation. Proceeding of the Second International Conference on Clean Coal Technologies for Our Future, Castiadas, Sardinia, Italy 2005. p. 10-2.
- [161] Gao N, Li A, Quan C. A novel reforming method for hydrogen production from biomass steam gasification. *Bioresour Technol.* 2009;100:4271-7.
- [162] Ockwig NW, Nenoff TM. Membranes for hydrogen separation. *Chem Rev.* 2007;107:4078-110.
- [163] Gallucci F, Fernandez E, Corengia P, van Sint Annaland M. Recent advances on membranes and membrane reactors for hydrogen production. *Chem Eng Sci.* 2013;92:40-66.
- [164] Ritter JA, Ebner AD. State - of - the - art adsorption and membrane separation processes for hydrogen production in the chemical and petrochemical industries. *Sep Sci Technol.* 2007;42:1123-93.
- [165] Üremek Cengiz N, Eren S, Sağlam M, Yüksel M, Ballice L. Influence of temperature and pressure on hydrogen and methane production in the hydrothermal gasification of wood residues. *J Supercrit Fluids.* 2016;107:243-9.
- [166] Bircan SY, Kamoshita H, Kanamori R, Ishida Y, Matsumoto K, Hasegawa Y, et al. Behavior of heteroatom compounds in hydrothermal gasification of biowaste for hydrogen production. *Appl Energy.* 2011;88:4874-8.
- [167] Chen Y, Guo L, Cao W, Jin H, Guo S, Zhang X. Hydrogen production by sewage sludge gasification in supercritical water with a fluidized bed reactor. *Int J Hydrogen Energy.* 2013;38:12991-9.

- [168] Nipattummakul N, Ahmed II, Kerdsuwan S, Gupta AK. Hydrogen and syngas production from sewage sludge via steam gasification. *Int J Hydrogen Energy*. 2010;35:11738-45.
- [169] Wang J, Cheng G, You Y, Xiao B, Liu S, He P, et al. Hydrogen-rich gas production by steam gasification of municipal solid waste (MSW) using NiO supported on modified dolomite. *Int J Hydrogen Energy*. 2012;37:6503-10.
- [170] Acharya B, Dutta A, Basu P. An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO. *Int J Hydrogen Energy*. 2010;35:1582-9.
- [171] Wu C, Williams PT. Pyrolysis-gasification of post-consumer municipal solid plastic waste for hydrogen production. *Int J Hydrogen Energy*. 2010;35:949-57.
- [172] Alvarez J, Kumagai S, Wu C, Yoshioka T, Bilbao J, Olazar M, et al. Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification. *Int J Hydrogen Energy*. 2014;39:10883-91.
- [173] Liu H, Grot S, Logan BE. Electrochemically Assisted Microbial Production of Hydrogen from Acetate. *Environ Sci Technol*. 2005;39:4317-20.
- [174] Rozendal RA, Hamelers HVM, Euverink GJW, Metz SJ, Buisman CJN. Principle and perspectives of hydrogen production through biocatalyzed electrolysis. *Int J Hydrogen Energy*. 2006;31:1632-40.
- [175] Heidrich ES, Dolfig J, Scott K, Edwards SR, Jones C, Curtis TP. Production of hydrogen from domestic wastewater in a pilot-scale microbial electrolysis cell. *Appl Microbiol Biotechnol*. 2013;97:6979-89.
- [176] Yossan S, Xiao L, Prasertsan P, He Z. Hydrogen production in microbial electrolysis cells: Choice of catholyte. *Int J Hydrogen Energy*. 2013;38:9619-24.

- [177] Luo S, Jain A, Aguilera A, He Z. Effective control of biohythane composition through operational strategies in an innovative microbial electrolysis cell. *Appl Energy*. 2017;206:879-86.
- [178] Wang A, Sun D, Cao G, Wang H, Ren N, Wu W-M, et al. Integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cells, and a microbial electrolysis cell. *Bioresour Technol*. 2011;102:4137-43.
- [179] Khan MZ, Nizami AS, Rehan M, Ouda OKM, Sultana S, Ismail IM, et al. Microbial electrolysis cells for hydrogen production and urban wastewater treatment: A case study of Saudi Arabia. *Appl Energy*. 2017;185:410-20.
- [180] Cotterill S, Heidrich E, Curtis T. 9 - Microbial electrolysis cells for hydrogen production. In: Scott K, Yu EH, editors. *Microbial Electrochemical and Fuel Cells*. Boston: Woodhead Publishing; 2016. p. 287-319.
- [181] Cusick RD, Kiely PD, Logan BE. A monetary comparison of energy recovered from microbial fuel cells and microbial electrolysis cells fed winery or domestic wastewaters. *Int J Hydrogen Energy*. 2010;35:8855-61.
- [182] Escapa A, Gil-Carrera L, García V, Morán A. Performance of a continuous flow microbial electrolysis cell (MEC) fed with domestic wastewater. *Bioresour Technol*. 2012;117:55-62.
- [183] Shen R, Jiang Y, Ge Z, Lu J, Zhang Y, Liu Z, et al. Microbial electrolysis treatment of post-hydrothermal liquefaction wastewater with hydrogen generation. *Appl Energy*. 2018;212:509-15.
- [184] Wagner RC, Regan JM, Oh S-E, Zuo Y, Logan BE. Hydrogen and methane production from swine wastewater using microbial electrolysis cells. *Water Res*. 2009;43:1480-8.

- [185] Tenca A, Cusick RD, Schievano A, Oberti R, Logan BE. Evaluation of low cost cathode materials for treatment of industrial and food processing wastewater using microbial electrolysis cells. *Int J Hydrogen Energy*. 2013;38:1859-65.
- [186] Dhar BR, Elbeshbishy E, Hafez H, Lee H-S. Hydrogen production from sugar beet juice using an integrated biohydrogen process of dark fermentation and microbial electrolysis cell. *Bioresour Technol*. 2015;198:223-30.
- [187] Liu W, Huang S, Zhou A, Zhou G, Ren N, Wang A, et al. Hydrogen generation in microbial electrolysis cell feeding with fermentation liquid of waste activated sludge. *Int J Hydrogen Energy*. 2012;37:13859-64.
- [188] Feng Y, Liu Y, Zhang Y. Enhancement of sludge decomposition and hydrogen production from waste activated sludge in a microbial electrolysis cell with cheap electrodes. *Environ Sci Water Res Technol*. 2015;1:761-8.
- [189] Li X-H, Liang D-W, Bai Y-X, Fan Y-T, Hou H-W. Enhanced H₂ production from corn stalk by integrating dark fermentation and single chamber microbial electrolysis cells with double anode arrangement. *Int J Hydrogen Energy*. 2014;39:8977-82.
- [190] Lu L, Ren N, Xing D, Logan BE. Hydrogen production with effluent from an ethanol-H₂-coproducing fermentation reactor using a single-chamber microbial electrolysis cell. *Biosens Bioelectron*. 2009;24:3055-60.
- [191] Patil SA, Harnisch F, Kapadnis B, Schröder U. Electroactive mixed culture biofilms in microbial bioelectrochemical systems: The role of temperature for biofilm formation and performance. *Biosens Bioelectron*. 2010;26:803-8.
- [192] Heidrich ES, Edwards SR, Dolfig J, Cotterill SE, Curtis TP. Performance of a pilot scale microbial electrolysis cell fed on domestic wastewater at ambient temperatures for a 12month period. *Bioresour Technol*. 2014;173:87-95.

- [193] Kadier A, Simayi Y, Kalil MS, Abdeslahian P, Hamid AA. A review of the substrates used in microbial electrolysis cells (MECs) for producing sustainable and clean hydrogen gas. *Renew Energy*. 2014;71:466-72.
- [194] Kokko M, Bayerköhler F, Erben J, Zengerle R, Kurz P, Kerzenmacher S. Molybdenum sulphides on carbon supports as electrocatalysts for hydrogen evolution in acidic industrial wastewater. *Appl Energy*. 2017;190:1221-33.
- [195] Sun R, Xing D, Jia J, Liu Q, Zhou A, Bai S, et al. Optimization of high-solid waste activated sludge concentration for hydrogen production in microbial electrolysis cells and microbial community diversity analysis. *Int J Hydrogen Energy*. 2014;39:19912-20.
- [196] Lu L, Xing D, Liu B, Ren N. Enhanced hydrogen production from waste activated sludge by cascade utilization of organic matter in microbial electrolysis cells. *Water Res*. 2012;46:1015-26.
- [197] Wang L, Liu W, Kang L, Yang C, Zhou A, Wang A. Enhanced biohydrogen production from waste activated sludge in combined strategy of chemical pretreatment and microbial electrolysis. *Int J Hydrogen Energy*. 2014;39:11913-9.
- [198] Chae K-J, Choi M-J, Kim K-Y, Ajayi FF, Chang I-S, Kim IS. Selective inhibition of methanogens for the improvement of biohydrogen production in microbial electrolysis cells. *Int J Hydrogen Energy*. 2010;35:13379-86.
- [199] Kadier A, Kalil MS, Chandrasekhar K, Mohanakrishna G, Saratale GD, Saratale RG, et al. Surpassing the current limitations of high purity H₂ production in microbial electrolysis cell (MECs): Strategies for inhibiting growth of methanogens. *Bioelectrochemistry*. 2018;119:211-9.

- [200] Lalaurette E, Thammannagowda S, Mohagheghi A, Maness P-C, Logan BE. Hydrogen production from cellulose in a two-stage process combining fermentation and electrohydrogenesis. *Int J Hydrogen Energy*. 2009;34:6201-10.
- [201] Cusick RD, Bryan B, Parker DS, Merrill MD, Mehanna M, Kiely PD, et al. Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater. *Appl Microbiol Biotechnol*. 2011;89:2053-63.
- [202] Catal T, Lesnik KL, Liu H. Suppression of methanogenesis for hydrogen production in single-chamber microbial electrolysis cells using various antibiotics. *Bioresour Technol*. 2015;187:77-83.
- [203] Hou Y, Luo H, Liu G, Zhang R, Li J, Fu S. Improved Hydrogen Production in the Microbial Electrolysis Cell by Inhibiting Methanogenesis Using Ultraviolet Irradiation. *Environ Sci Technol*. 2014;48:10482-8.
- [204] Wang Y, Guo W-Q, Xing D-F, Chang J-S, Ren N-Q. Hydrogen production using biocathode single-chamber microbial electrolysis cells fed by molasses wastewater at low temperature. *Int J Hydrogen Energy*. 2014;39:19369-75.
- [205] Ajayi FF, Kim K-Y, Chae K-J, Choi M-J, Kim IS. Effect of hydrodynamic force and prolonged oxygen exposure on the performance of anodic biofilm in microbial electrolysis cells. *Int J Hydrogen Energy*. 2010;35:3206-13.
- [206] Ali J, Sohail A, Wang L, Rizwan Haider M, Mulk S, Pan G. Electro-Microbiology as a Promising Approach Towards Renewable Energy and Environmental Sustainability. *Energies*. 2018;11.
- [207] Zhen G, Lu X, Kumar G, Bakonyi P, Xu K, Zhao Y. Microbial electrolysis cell platform for simultaneous waste biorefinery and clean electrofuels generation: Current situation, challenges and future perspectives. *Prog Energy Combust Sci*. 2017;63:119-45.

- [208] Kumar R, Singh L, Zularisam AW. Exoelectrogens: Recent advances in molecular drivers involved in extracellular electron transfer and strategies used to improve it for microbial fuel cell applications. *Renew Sust Energy Rev.* 2016;56:1322-36.
- [209] Karthikeyan R, Cheng KY, Selvam A, Bose A, Wong JWC. Bioelectrohydrogenesis and inhibition of methanogenic activity in microbial electrolysis cells - A review. *Biotechnol Adv.* 2017;35:758-71.
- [210] Rago L, Baeza JA, Guisasola A. Increased performance of hydrogen production in microbial electrolysis cells under alkaline conditions. *Bioelectrochemistry.* 2016;109:57-62.
- [211] Lewis AJ, Borole AP. Microbial electrolysis cells using complex substrates achieve high performance via continuous feeding-based control of reactor concentrations and community structure. *Appl Energy.* 2019;240:608-16.
- [212] Shen R, Liu Z, He Y, Zhang Y, Lu J, Zhu Z, et al. Microbial electrolysis cell to treat hydrothermal liquefied wastewater from cornstalk and recover hydrogen: Degradation of organic compounds and characterization of microbial community. *Int J Hydrogen Energy.* 2016;41:4132-42.
- [213] Tong H, Shen Y, Zhang J, Wang C-H, Ge TS, Tong YW. A comparative life cycle assessment on four waste-to-energy scenarios for food waste generated in eateries. *Appl Energy.* 2018;225:1143-57.
- [214] ISO E. 14040: 2006. Environmental management-Life cycle assessment-Principles and framework. 2006.
- [215] ISO E. 14044: 2006. Environmental management-Life cycle assessment-Requirements and guidelines. 2006.

- [216] Ochs D, Wukovits W, Ahrer W. Life cycle inventory analysis of biological hydrogen production by thermophilic and photo fermentation of potato steam peels (PSP). *J Cleaner Prod.* 2010;18:S88-S94.
- [217] Djomo SN, Blumberga D. Comparative life cycle assessment of three biohydrogen pathways. *Bioresour Technol.* 2011;102:2684-94.
- [218] Ferreira AF, Ortigueira J, Alves L, Gouveia L, Moura P, Silva C. Biohydrogen production from microalgal biomass: Energy requirement, CO₂ emissions and scale-up scenarios. *Bioresour Technol.* 2013;144:156-64.
- [219] Ferreira AF, Ortigueira J, Alves L, Gouveia L, Moura P, Silva CM. Energy requirement and CO₂ emissions of bioH₂ production from microalgal biomass. *Biomass Bioenergy.* 2013;49:249-59.
- [220] Pacheco R, Ferreira AF, Pinto T, Nobre BP, Loureiro D, Moura P, et al. The production of pigments & hydrogen through a *Spirogyra* sp. biorefinery. *Energy Convers Manage.* 2015;89:789-97.
- [221] Khoo HH. Life cycle impact assessment of various waste conversion technologies. *Waste Manage.* 2009;29:1892-900.
- [222] Hwang JJ, Chang WR. Life-cycle analysis of greenhouse gas emission and energy efficiency of hydrogen fuel cell scooters. *Int J Hydrogen Energy.* 2010;35:11947-56.
- [223] Tock L, Maréchal F. Co-production of hydrogen and electricity from lignocellulosic biomass: Process design and thermo-economic optimization. *Energy.* 2012;45:339-49.
- [224] Wulf C, Kaltschmitt M. Life cycle assessment of hydrogen supply chain with special attention on hydrogen refuelling stations. *Int J Hydrogen Energy.* 2012;37:16711-21.

- [225] Bartolozzi I, Rizzi F, Frey M. Comparison between hydrogen and electric vehicles by life cycle assessment: A case study in Tuscany, Italy. *Appl Energy*. 2013;101:103-11.
- [226] Moreno J, Dufour J. Life cycle assessment of hydrogen production from biomass gasification. Evaluation of different Spanish feedstocks. *Int J Hydrogen Energy*. 2013;38:7616-22.
- [227] Susmozas A, Iribarren D, Dufour J. Life-cycle performance of indirect biomass gasification as a green alternative to steam methane reforming for hydrogen production. *Int J Hydrogen Energy*. 2013;38:9961-72.
- [228] Muresan M, Cormos CC, Agachi PS. Comparative life cycle analysis for gasification-based hydrogen production systems. *J Renewable Sustainable Energy*. 2014;6:013131.
- [229] Iribarren D, Susmozas A, Petrakopoulou F, Dufour J. Environmental and exergetic evaluation of hydrogen production via lignocellulosic biomass gasification. *J Cleaner Prod*. 2014;69:165-75.
- [230] Galera S, Gutiérrez Ortiz FJ. Life cycle assessment of hydrogen and power production by supercritical water reforming of glycerol. *Energy Convers Manage*. 2015;96:637-45.
- [231] Martín-Gamboa M, Iribarren D, Susmozas A, Dufour J. Delving into sensible measures to enhance the environmental performance of biohydrogen: A quantitative approach based on process simulation, life cycle assessment and data envelopment analysis. *Bioresour Technol*. 2016;214:376-85.
- [232] Susmozas A, Iribarren D, Zapp P, Linßen J, Dufour J. Life-cycle performance of hydrogen production via indirect biomass gasification with CO₂ capture. *Int J Hydrogen Energy*. 2016;41:19484-91.

- [233] Hendrawan, Dowaki K, Mori S. Life cycle inventory analysis of waste wood to hydrogen for domestic energy sector: Case study: Indonesia. 2017 International Conference on Green Energy and Applications (ICGEA)2017. p. 130-3.
- [234] García CA, Morales M, Quintero J, Aroca G, Cardona CA. Environmental assessment of hydrogen production based on *Pinus patula* plantations in Colombia. *Energy*. 2017;139:606-16.
- [235] Rajabi Hamedani S, Villarini M, Colantoni A, Moretti M, Bocci E. Life Cycle Performance of Hydrogen Production via Agro-Industrial Residue Gasification—A Small Scale Power Plant Study. *Energies*. 2018;11.
- [236] Salkuyeh YK, Saville BA, MacLean HL. Techno-economic analysis and life cycle assessment of hydrogen production from different biomass gasification processes. *Int J Hydrogen Energy*. 2018;43:9514-28.
- [237] Nogueira Junior E, Kumar M, Pankratz S, Oyedun AO, Kumar A. Development of life cycle water footprints for the production of fuels and chemicals from algae biomass. *Water Res*. 2018;140:311-22.
- [238] Suwanmanee U, Saebea D, Hacker V, Assabumrungrat S, Arpornwichanop A, Authayanun S. Conceptual design and life cycle assessment of decentralized power generation by HT-PEMFC system with sorption enhanced water gas shift loop. *Energy Convers Manage*. 2018;171:20-30.
- [239] Mehmeti A, Angelis-Dimakis A, Arampatzis G, McPhail JS, Ulgiati S. Life Cycle Assessment and Water Footprint of Hydrogen Production Methods: From Conventional to Emerging Technologies. *Environments*. 2018;5.
- [240] Siddiqui O, Dincer I. A well to pump life cycle environmental impact assessment of some hydrogen production routes. *Int J Hydrogen Energy*. 2019;44:5773-86.

- [241] Chen J, Xu W, Zuo H, Wu X, E J, Wang T, et al. System development and environmental performance analysis of a solar-driven supercritical water gasification pilot plant for hydrogen production using life cycle assessment approach. *Energy Convers Manage*. 2019;184:60-73.
- [242] Wang C, Jin H, Peng P, Chen J. Thermodynamics and LCA analysis of biomass supercritical water gasification system using external recycle of liquid residual. *Renew Energy*. 2019;141:1117-26.
- [243] Chen J, Xu W, Wu X, E J, Lu N, Wang T, et al. System development and environmental performance analysis of a pilot scale microbial electrolysis cell for hydrogen production using urban wastewater. *Energy Convers Manage*. 2019;193:52-63.
- [244] Huijbregts MAJ, Steinmann ZJN, Elshout PMF, Stam G, Verones F, Vieira M, et al. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. *Int J Life Cycle Assess*. 2017;22:138-47.
- [245] Dufour J, Serrano DP, Gálvez JL, González A, Soria E, Fierro JLG. Life cycle assessment of alternatives for hydrogen production from renewable and fossil sources. *Int J Hydrogen Energy*. 2012;37:1173-83.
- [246] Verma A, Kumar A. Life cycle assessment of hydrogen production from underground coal gasification. *Appl Energy*. 2015;147:556-68.
- [247] Hajjaji N, Pons M-N, Renaudin V, Houas A. Comparative life cycle assessment of eight alternatives for hydrogen production from renewable and fossil feedstock. *J Cleaner Prod*. 2013;44:177-89.
- [248] Albini E, Bacchi D, Ferrara G, Francini G, Galoppi G, Lombardi L, et al. Bioenergy recovery from waste: comparison of different treatment scenarios by LCA. *Energy Procedia*. 2018;148:34-41.

- [249] Escamilla-Alvarado C, Poggi-Varaldo HM, Ponce-Noyola MT. Bioenergy and bioproducts from municipal organic waste as alternative to landfilling: a comparative life cycle assessment with prospective application to Mexico. *Environ Sci Pollut Res*. 2017;24:25602-17.
- [250] Ren J, Toniolo S. Life cycle sustainability decision-support framework for ranking of hydrogen production pathways under uncertainties: An interval multi-criteria decision making approach. *J Cleaner Prod*. 2018;175:222-36.
- [251] Valente A, Iribarren D, Dufour J. Life cycle sustainability assessment of hydrogen from biomass gasification: A comparison with conventional hydrogen. *Int J Hydrogen Energy*. 2019.
- [252] Francmanis E, Khabdullin A, Khabdullin A, Khabdullina Z, Khabdullina G, Gusca J. Comparative Environmental Analysis of Microbial Electrochemical Systems. *Energy Procedia*. 2016;95:564-8.
- [253] Streeck J, Hank C, Neuner M, Gil-Carrera L, Kokko M, Pauliuk S, et al. Bio-electrochemical conversion of industrial wastewater-COD combined with downstream methanol synthesis – an economic and life cycle assessment. *Green Chem*. 2018;20:2742-62.
- [254] Zhang J, Yuan H, Abu-Reesh IM, He Z, Yuan C. Life Cycle Environmental Impact Comparison of Bioelectrochemical Systems for Wastewater Treatment. *Procedia CIRP*. 2019;80:382-8.
- [255] Foley JM, Rozendal RA, Hertle CK, Lant PA, Rabaey K. Life Cycle Assessment of High-Rate Anaerobic Treatment, Microbial Fuel Cells, and Microbial Electrolysis Cells. *Environ Sci Technol*. 2010;44:3629-37.

- [256] Igos E, Besson M, Navarrete Gutiérrez T, Bisinella de Faria AB, Benetto E, Barna L, et al. Assessment of environmental impacts and operational costs of the implementation of an innovative source-separated urine treatment. *Water Res.* 2017;126:50-9.
- [257] Lee H-S, Vermaas WFJ, Rittmann BE. Biological hydrogen production: prospects and challenges. *Trends Biotechnol.* 2010;28:262-71.
- [258] Tapia-Venegas E, Ramirez-Morales JE, Silva-Illanes F, Toledo-Alarcón J, Paillet F, Escudie R, et al. Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. *Rev Environ Sci Bio.* 2015;14:761-85.
- [259] Rivera I, Schröder U, Patil SA. Chapter 5.8 - Microbial Electrolysis for Biohydrogen Production: Technical Aspects and Scale-Up Experiences. In: Mohan SV, Varjani S, Pandey A, editors. *Microbial Electrochemical Technology*; Elsevier; 2019. p. 871-98.
- [260] Schievano A, Sciarria TP, Gao YC, Scaglia B, Salati S, Zanardo M, et al. Dark fermentation, anaerobic digestion and microbial fuel cells: An integrated system to valorize swine manure and rice bran. *Waste Manage.* 2016;56:519-29.