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1 **Techno-economic and environmental impact assessment of**  
2 **hydrogen production processes using bio-waste as renewable**  
3 **energy resource**

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25 **Abstract**

26 There is a wide spectrum of biological wastes, from which H<sub>2</sub> production can generate clean  
27 energy while minimizing environmental degradation. This study aims to conduct techno-  
28 economic and environmental impact assessment of major hydrogen production processes such  
29 as dark, photo and solid-state fermentation, microbial electrolysis cell (MEC), gasification,  
30 pyrolysis and plasma. From the technological point of view, the dark fermentation has shown  
31 better performance in comparison to the other processes. However, the hybrid dark  
32 fermentation with photo-fermentation and MEC has shown higher performances with around  
33 1 L H<sub>2</sub>/g organic waste. Regarding the economic aspect, the cheapest H<sub>2</sub> production belongs to  
34 gasification and fermentation with approximately 2 US\$/g and 2.3 US\$/g followed by plasma  
35 (2.4 US\$/g), pyrolysis (2.6 US\$/g), MEC (2.8 US\$/g), and photo-fermentation (3.5 US\$/g).  
36 Regarding the potential environmental impact, the fermentation process showed the lowest  
37 greenhouse gas emission with 15 kg CO<sub>2</sub>-eq/kg hydrogen followed by gasification, MEC and  
38 plasma. Regarding the potential commercial applications, gasification is the most mature with  
39 the highest possible technology readiness at level 9.

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42 *Keywords:* Hydrogen; Techno-economic analysis; Life cycle analysis; Fermentation; Microbial  
43 electrolysis cell; Gasification

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45 **Word count: 9051**

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## 50 **Highlights**

- 51 • Potential processes for H<sub>2</sub> production from bio-wastes were critically reviewed.
- 52 • Techno-economic, efficiency and life cycle analyses of the processes were conducted.
- 53 • Hybrid processes showed cheaper and cleaner H<sub>2</sub> production than single process.
- 54 • Dark fermentation with microbial electrolysis cell demonstrated best performance.

55

## 56 **Abbreviations**

57	acetyl-CoA	acetyl coenzyme A
58	AD	anaerobic digestion
59	ANFIS	adaptive network-based fuzzy inference system
60	ANN	artificial neural network
61	ATP	adenosine triphosphate
62	CFD	computational fluid dynamics
63	COD	chemical oxygen demand
64	DAEM	distributed activation energy model
65	EF	entrained flow
66	FB	fluidized bed
67	GHG	greenhouse gases
68	HCs	hydrocarbons
69	HRT	hydraulic retention time
70	LCA	life cycle analysis
71	LCOH	levelized cost of hydrogen
72	MEC	microbial electrolysis cell
73	MSW	municipal solid waste
74	OLR	organic loading rate

75	PAHs	polycyclic aromatic hydrocarbons
76	PM	particulate matter
77	PMW	paper mill waste
78	SSF	solid-state fermentation
79	VFAs	volatile fatty acids
80	VS	volatile solid
81	TEA	techno-economic analysis
82	TRL	technology readiness level

83

## 84 **1. Introduction**

85 With the rapid urbanization, industrialization and population growth, the global energy  
86 requirement is estimated to increase by 56% from 553 quadrillion kJ to 855 quadrillion kJ  
87 during 2010-2040 [1, 2]. As the dominant energy sources, fossil fuels such as coal and  
88 petroleum are regarded as nonrenewable energy . In addition, the combustion of fossil fuels in  
89 power generation and transport emits various pollutants including greenhouse gases (GHG),  
90 carbon monoxide, nitrogen oxides, particulate matter (PM) and organic pollutants such as  
91 polycyclic aromatic hydrocarbons (PAHs) into the atmosphere [3-5]. The global warming from  
92 GHG emissions has caused different types of detrimental effects on human wellbeing in all  
93 continents, e.g. undernutrition and mental health effects from droughts and floods in South  
94 Africa, Ethiopia, Bangladesh and China along with respiratory and cardiovascular impacts of  
95 record heatwaves and wildfires in western Europe, western North America and Australia [5].  
96 Climate change has become a threat for many foundations of wellbeing and human health over  
97 a long period of time [6, 7]. The emitted pollutants are not only toxic and even carcinogenic,  
98 but also can induce secondary organic aerosols with human health implications [7, 8]. Such  
99 adverse effects are most felt in urban areas with a high density of human population, as it is

100 estimated that vehicle emissions are responsible for an estimated 385000 premature deaths and  
101 US\$1 trillion of health damage globally in 2015 [9].

102 Currently, approximately 64% of the gross inland consumption of renewable energy in the  
103 European Union belongs to bioenergy [10]. It is expected that renewable energy production  
104 will contribute approximately 51% of the total energy requirements globally by 2040, and  
105 become the dominating energy source in the next decade [11]. In addition, freshwater shortage  
106 is regarded as another severe problem of the world today [1, 12]. Moreover, solid waste and  
107 wastewater are considered as the most severe environmental problems today [12-15], yet they  
108 can provide valuable sources of biomasses for the recovery of energy [15]. There is a wide  
109 range of technologies to manage each of these challenges separately, e.g. by applying  
110 composting and vermicomposting processes for waste disposal [14, 16], advanced oxidation  
111 processes [17-19] for water and wastewater treatment, and energy generation from renewable  
112 energy resources like wind and wave [20]. However, the development of processes by which  
113 water and energy shortages together with environmental and health problems of wastes such  
114 as municipal solid waste (MSW) can be simultaneously addressed is exciting and urgently  
115 needed [21].

116 Hydrogen is a very interesting energy carrier with an energy yield of 122 kJ/g that is 2.75  
117 times more than the fossil fuels. Hydrogen as a clean energy is free of CO<sub>2</sub> and any toxic  
118 emissions during combustion, with water as the final product. In fact, the application of  
119 hydrogen as a fuel meets the zero-emission target which is now globally pursued. Hydrogen  
120 can be produced from biomass and renewable sources, and more attentions have been attracted  
121 towards the generation of hydrogen from wastes and wastewater [7, 22]. There are various  
122 technologies for the production of hydrogen from wastes and wastewater, i.e. photo [22], dark  
123 and solid-state fermentation (SSF) [23], microbial electrolysis cell (MEC) [1], pyrolysis [24],  
124 gasification [25] and plasma [26]. These processes have been studied for different types of

125 solid and liquid wastes; however, there is still a knowledge gap regarding which process is the  
 126 best option for hydrogen production and treatment efficiency from the full techno-economic  
 127 analysis (TEA) and environmental impact analysis. Table 1 compares this review article and  
 128 other related published review papers. Although other papers have examined different aspects  
 129 of H<sub>2</sub> production in various processes, the emerging processes for H<sub>2</sub> production, e.g. SSF,  
 130 MEC and plasma were less studied in techno-economic and environmental impact analysis.  
 131 Furthermore, current information about the TEA and environmental aspects in more mature  
 132 processes like pyrolysis and gasification is insufficient to allow the selection of the best process  
 133 for H<sub>2</sub> production from different types of bio-wastes.

134 **Table 1.**

135 Comparison of this study with other review articles on hydrogen production as renewable  
 136 energy.

Process	Evaluation	Reference							
		[27]	[28]	[29]	[30]	[31]	[32]	[33]	This study
Dark fermentation	Efficiency analysis	×	√	√	×	×	×	×	√
	TEA	×	×	×	×	×	√	×	√
	LCA	×	×	×	×	×	×	×	√
	Bio-waste	×	√	√	×	×	√	×	√
Photo fermentation	Efficiency analysis	×	×	×	×	×	×	×	√
	TEA	×	×	×	×	×	√	×	√
	LCA	×	×	×	×	×	×	×	√
	Bio-waste	×	×	×	×	×	√	×	√
SSF	Efficiency analysis	×	×	×	×	×	×	×	√
	TEA	×	×	×	×	×	×	×	√
	LCA	×	×	×	×	×	×	×	√
	Bio-waste	×	×	×	×	×	×	×	√
MEC	Efficiency analysis	×	×	×	×	×	×	×	√
	TEA	×	×	×	×	×	×	×	√
	LCA	×	×	×	×	×	×	×	√
	Bio-waste	×	×	×	×	×	×	×	√
Pyrolysis	Efficiency analysis	×	×	×	×	×	√	√	√

	TEA	×	×	×	×	×	√	×	√
	LCA	×	×	×	×	×	×	×	√
	Bio-waste	×	×	×	×	×	√	√	√
	Efficiency analysis	×	×	×	√	×	√	√	√
Gasification	TEA	×	×	×	√	×	√	√	√
	LCA	×	×	×	×	×	×	√	√
	Bio-waste	√	×	×	√	×	√	√	√
	Efficiency analysis	×	×	×	×	×	×	√	√
Plasma	TEA	×	×	×	×	×	×	√	√
	LCA	×	×	×	×	×	×	×	√
	Bio-waste	×	×	×	×	×	×	√	√
Other H <sub>2</sub> production processes studied		√	×	×	√	√	√	√	√
Comprehensive appraisal of all processes		×	×	×	×	×	×	×	√

137



138 This study aims to address the mechanisms, technical and operating conditions, economic and  
139 environmental aspects of common and emerging hydrogen production processes from wastes  
140 and wastewater, including photo fermentation, dark fermentation, solid fermentation, MEC,  
141 pyrolysis, gasification, and plasma processes. Based on the advantages, disadvantages and  
142 capabilities of these processes, the best process will be recommended for further research and  
143 commercial exploitation.

144

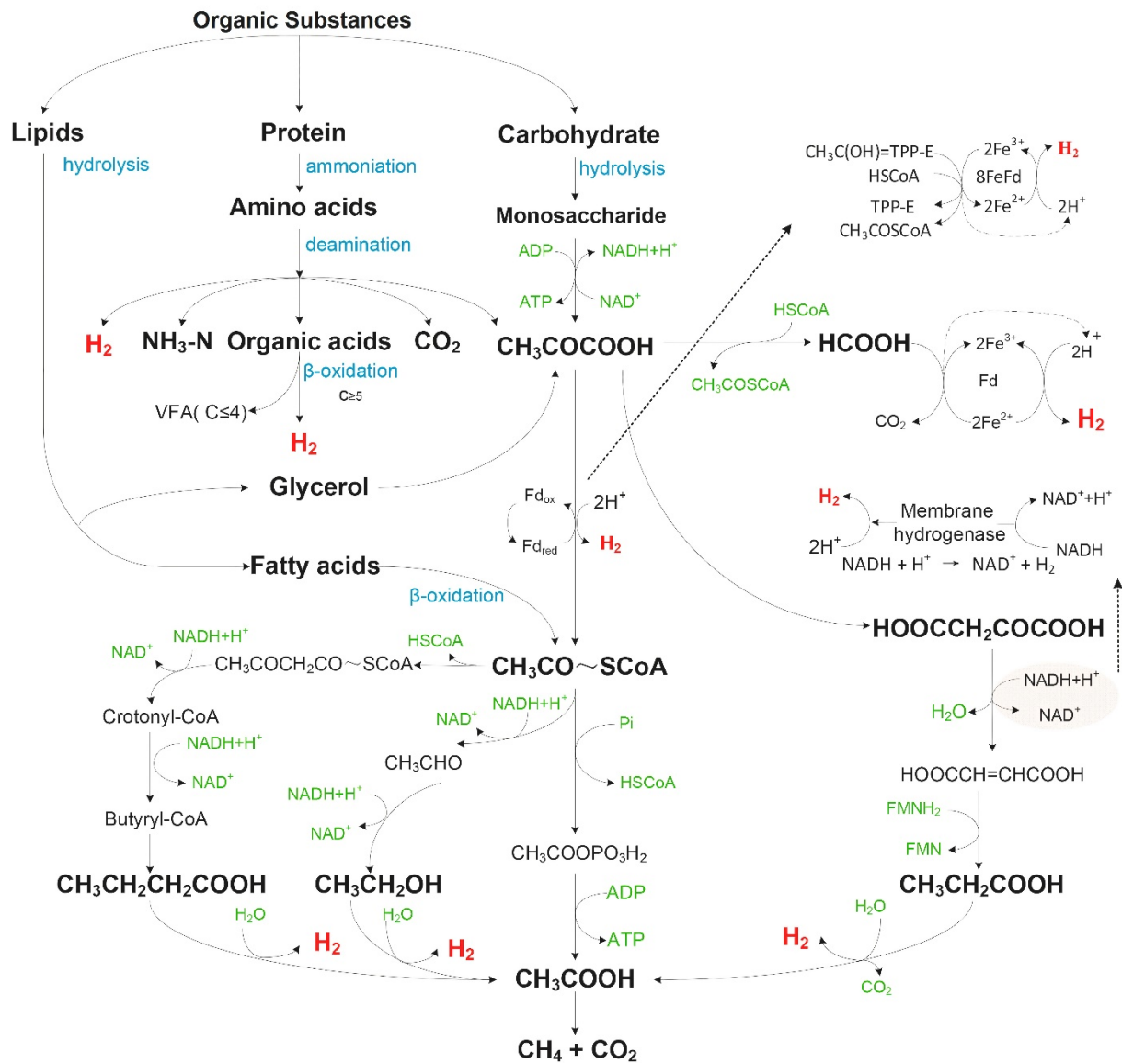
## 145 **2. Technical analysis of hydrogen production processes from wastes**

### 146 *2.1. Dark, photo and solid-state fermentation*

147 Anaerobic biological processes such as anaerobic digestion (AD), which normally consist of  
148 four different stages including hydrolysis, acidogenesis, acetogenesis and methanogenesis, are  
149 regarded as one of the most effective processes for both treatment of the wastes and energy  
150 production [34]. Acidogenic fermentation, which is conducted using a consortium of  
151 microorganisms and includes only first three stages of the anaerobic biological process, plays  
152 a vital role during this process by linking the hydrolysis and methanogenesis stages [34, 35]. In  
153 order to produce acidogenic products, syntrophic activities of the microorganisms in anaerobic  
154 processes play an important role, by syntrophically degrading the organic matter into hydrogen  
155 and other acidogenic phase products. Since a wide spectrum of the microorganisms are used  
156 and there are different pathways in this process, interspecies transfer of mass and electron is  
157 one of the key mechanisms for hydrogen and fatty acid production in such communities [34].  
158 The mechanisms of the organic matter degradation in dark fermentation process as well as H<sub>2</sub>  
159 production are demonstrated in Fig. 1.

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163

164 **Fig. 1.** Hydrogen production pathways by fermentation process from organic substances.

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168 As observed in Fig. 1, different types of organic matter can potentially be converted into

169  $\text{H}_2$  by fermentation. However, the conversion of the different types of organic matter can be

170 carried out through different pathways with different energy outputs. The shortest pathways to

171 produce  $\text{H}_2$  from organic matter are *via*  $\beta$ -oxidation of organic acids, and deamination of the

172 amino acids. The other  $\text{H}_2$  production pathway, which is dominant with *Clostridium* spp., is the

173 decarboxylation of pyruvate through ferredoxin enzyme. During the glycolysis of amino acids  
174 and carbohydrates, pyruvate is produced and degraded to acetyl-CoA, the generated electrons  
175 over this process could react with protons and generate H<sub>2</sub>. Facultative anaerobes dominantly  
176 produce H<sub>2</sub> through format cleavage as well [36]. In addition, the required adenosine  
177 triphosphate (ATP) and energy obtained from proton gradient process are also indicated in Fig.  
178 1.

179 After the dark fermentation process, there is a great proportion of volatile fatty acids  
180 (VFAs) in the system, which can be used by photosynthetic bacteria to recover more hydrogen  
181 from organic matter. Purple non-sulfur bacteria, which are able to gain electrons from VFAs to  
182 generate H<sub>2</sub>, are regarded as the most dominant photosynthetic bacteria investigated in photo-  
183 fermentation processes. In these processes, ubiquinone transports the produced electrons from  
184 the oxidation of organic matter to the photosystem. Subsequently, the light energizes the  
185 transported electrons, which are cycled in electron transport chain of photosynthetic system  
186 resulting in more proton gradients. Finally, oxidoreductase transfers the electrons to ferredoxin  
187 which is applied to generate H<sub>2</sub> by nitrogenase. This process is considered as photo-  
188 fermentation process, which has been suggested to combine with dark fermentation to produce  
189 more H<sub>2</sub> [36].

190 SSF process operates in the same way as the dark fermentation process with almost zero  
191 free water [37]. Since the proportion of the biomass in SSF is higher than that of the submerged  
192 fermentation, the productivity of SSF is enhanced. Therefore, SSF is considered as more  
193 economic from the aspect of capital and operating costs. The main challenges of SSF are the  
194 determination of the microbial biomass, product recovery and scale-up operation [38].

195 These three processes have been widely applied for H<sub>2</sub> production from different types of  
196 wastes. However, these processes have shown various performances under different operation  
197 conditions. Table 2 summarizes the operating conditions as well as the performance of these  
198 processes in H<sub>2</sub> production and waste treatment efficiency.

199 As shown in Tables 2 and 3, the proportions of the H<sub>2</sub> produced by the integrated dark and  
200 photo fermentation processes are higher than separate dark and photo fermentations. In  
201 addition, single dark fermentation has demonstrated better performance in the production of H<sub>2</sub>  
202 from wastes compared with single photo fermentation processes. Apart from the effectiveness  
203 of the different types of the fermentation processes in H<sub>2</sub> production from wastes, the type of  
204 the waste used is a very important factor. For example, as observed in Fig. 1, the type of the  
205 wastes plays a key role to determine the metabolic pathways of the organic matter resulting in  
206 variable extent and rates of H<sub>2</sub> production. It has been reported that 2-4 mol H<sub>2</sub>/mol hexose can  
207 theoretically be produced by dark fermentation. The proportions of the various VFAs produced  
208 during dark fermentation, which are affected by diverse factors particularly type of the wastes,  
209 are very effective in more exact proportion of 2-4 mol H<sub>2</sub>/mol hexose range [39].

210 In addition, as can be observed in Tables 2 and 3, the biodegradability of the wastes is  
211 another key factor affecting this process. In addition, the type of the microbial community,  
212 hydraulic retention time (HRT), temperature, organic loading rate (OLR) and pH are some of  
213 the other important parameters impacting fermentation process performance [40-42].

214 As shown in Table 2, limited removal efficiency of chemical oxygen demand (COD) is  
215 regarded as the most critical drawback in this process. This parameter can particularly be very  
216 challenging in wastewater treatment. Therefore, the integration of the fermentation and other  
217 processes, e.g. fermentation and membrane technology, dark and photo fermentation are  
218 regarded as the applicable solutions to tackle this challenge. Furthermore, the combination and  
219 hybridization of dark fermentation process with other different processes [36], along with the  
220 optimization of the operating conditions through different procedures, e.g. the advanced models  
221 are regarded as the other future research trends for this process [36, 43-45]

222 **Table 2.**  
 223 The operating conditions and performances of dark fermentation process.

Process	Bio-waste	Inoculum	Temp. (°C)	pH	HRT	OLR	COD removal efficiency	H <sub>2</sub> production	Reference
Dark fermentation	Manure and food waste	Activated anaerobic sludge	55	6.5	48 h	28.2 g volatile solid (VS)/d	-	16.5 mL H <sub>2</sub> /g VS	[40]
Dark fermentation	Food waste (Melon residues)	Activated anaerobic sludge	25	5.6-5.8	20 & 27 h	107.6 g/L	21%	395.5 mL H <sub>2</sub> /g VS	[35]
Dark fermentation	Food wastes (mixed fruit wastes)	Activated anaerobic sludge	55	5	5 d	-	-	553 mL H <sub>2</sub> /g VS	[41]
Dark fermentation	Food waste	Activated anaerobic sludge	37	6	0.7-1.2 d	150 g COD/L	-	17 mL H <sub>2</sub> /g VS	[46]
Dark fermentation	Food waste and white mud from ammonia-soda process	Sewage Sludge	55	5.5	36 h	270.6 g/L.d	-	145.4 mL H <sub>2</sub> /g VS	[47]
Dark fermentation	Pig manure	Activated anaerobic sludge	55	5	24 h	48.2 g VS/L.d	-	96.4 mL H <sub>2</sub> /g VS	[42]
Dark fermentation	Cow dung	Manure	60	6.6-5.4	8 d	-	-	0.743 mL H <sub>2</sub> /g cow dung	[48]
Dark fermentation	Corn stalk	Cow dung compost	36	7	-	-	-	144.3 mL H <sub>2</sub> /g corn stalk	[49]
Dark fermentation	Cheese whey and buffalo manure	Anaerobic digested sludge	55	4.8-5	12 d	2.1 g VS/L.d	-	152.2 mL H <sub>2</sub> /g VS	[50]
Dark fermentation	Pig manure and rice straw	Anaerobic digested sludge	55	5-5.5	4.5 d	-	18%	44.59 mL H <sub>2</sub> /g VS	[51]
Dark fermentation	Swine manure	Mixed culture of fermentative bacteria	37	5	16 h	-	-	830 mL H <sub>2</sub> /g VS	[52]

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227 **Table 3.**

228 The operating conditions and performances of photo and combined dark-photo fermentation processes.

Process	Bio-waste	Inoculum		Temp. (°C)		pH		HRT (h)		Light intensity (Lux)	H <sub>2</sub> production			Reference
		Dark	Photo	dark	photo	dark	photo	dark	photo		Dark fermentation	Photo-fermentation	Total	
Photo-fermentation	Corn Stover	-	Photosynthetic bacteria HAU-M1	-	30	-	6.5	-	120	7000	-	58 mL H <sub>2</sub> /g VS	58 mL H <sub>2</sub> /g VS	[53]
Dark and photo-fermentation	Cassava	Cattle dung compost	<i>R. sphaeroides</i>	37	30	6.8	7	72	268	4000	199 mL H <sub>2</sub> /g cassava	611 mL H <sub>2</sub> /g cassava	810 mL H <sub>2</sub> /g cassava	[39]
Dark and photo-fermentation	Food waste	Cattle dung compost	<i>R. sphaeroides</i>	37	30			72	168	4000	220 mL H <sub>2</sub> /g food waste	451 mL H <sub>2</sub> /g food waste	671 mL H <sub>2</sub> /g food waste	[39]
Dark and photo-fermentation	Cassava starch	mixed anaerobic bacteria	Mixed photosynthetic bacteria	31	30	6.3	7	-	-	6000	351 mL H <sub>2</sub> /g starch	489 mL H <sub>2</sub> /g starch	840 mL H <sub>2</sub> /g starch	[54]
Dark and photo-fermentation	<i>Chlorella sp.</i> biomass	Anaerobic sludge	PNSB <i>Rhodobacter sphaeroides</i> TISTR 1952	35	37	6	7	4.7	0.23	5000	47.2 mL H <sub>2</sub> /g VS	125 mL H <sub>2</sub> /g VS	172.5 mL H <sub>2</sub> /g VS	[55]

229

## 230 2.2. *Microbial electrolysis cell*

231 MEC is a process in which electro-genic microorganisms utilize substrate to generate  
232 hydrogen. Single and double chamber reactors are two common types of configurations for  
233 MEC. Two electrodes as anode and cathode are installed in the related chambers and linked  
234 using an external circuit. The substrate present in wastewater is consumed by some electro-  
235 genic bacteria producing electrons and transfer to the anode by two general mechanisms, i.e.  
236 indirect and direct electron transfer. The first one is carried out by soluble mediators, and the  
237 second one is conducted by nanowires and membrane proteins. Coulombic efficiency as well  
238 as cathodic hydrogen recovery, which are the ratio of the potential electrons recovered from  
239 organic matters to the actual one in anode and the ratio of the potential hydrogen recovered in  
240 cathode to the actual one respectively, are two of the vital factors affected by different operating  
241 parameters [1]. Mild operation conditions are regarded as one of the important merits of MECs;  
242 however, by virtue of some barriers, e.g. thermodynamic and further energy requirement, the  
243 MEC cannot automatically run. Therefore, limited power (0.11 V) is required to run the MECs  
244 for hydrogen generation from acetate which is 10% lower than the usual required power for  
245 water electrolysis (1.23-2 V) [56]. This process is regarded as an emerging and high potential  
246 process with some limitations for scaling up like less mass transfer and energy loss [56, 57].  
247 The challenges of this process are classified in five different categories, i.e. anode  
248 (methanogenic electron losses, electrode resistance and metabolic diversity), cell design  
249 (complex wiring, single vs two chambered, stack configuration and scale-up), power source  
250 (using high carbon footprint electrical energy and external energy demand), membrane (long-  
251 term stability, bio-fouling, pH imbalance, high cost, substrate and gas crossovers) and cathode  
252 (side reaction, long-term stability, electrode resistance and high catalyst cost). Tackling all of  
253 these challenges to improve the efficiency of the process is the future research trend of this  
254 process. In addition, great capability of this process for coupling with different other processes

255 to produce more and sustainable energy [56, 58] as well as application of new and robust  
256 models are recognized as different items for future research trend in this field [1].

257 As presented in Table 4, high rate of H<sub>2</sub> production and treatment efficiency belong to  
258 MEC processes using fermentation liquid as influent. In fact, the best results were obtained  
259 using a combined fermentation and MEC process [58]. Therefore, similar to the fermentation  
260 process, the hybrid MEC processes showed great performance in both H<sub>2</sub> production and waste  
261 treatment efficiency.

262

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265



266 **Table 4.**

267 The operating conditions and performances of single MEC and hybridized MEC/AD processes.

Process		Bio-waste	Inoculum	Temp. (°C)	pH	Influent COD (mg/L)	COD removal (%)	H <sub>2</sub> production	Reference
Overall process	Sub-process								
AD-MEC		Fermentation liquid of waste activated sludge	Aeration tank effluent	22	7	6458	Up to 60	1200 mL/g COD	[59]
MEC-dark fermentation	Dark fermentation	Corn stalk	Cow dung compost	36	7	20000	-	129.8 mL/g corn stalk	[60]
	MEC	Effluent from dark fermentation	Fermentation bioreactor	36	7	3000-12000	44	257.3 mL/g corn stalk	
AD-MEC	AD	Food waste	Anaerobic granular sludge				26.1	49.4 mL/g VS	[58]
	AD-MEC	Food waste	Anaerobic granular sludge	30	6.5-7.5	2500-3500	34.9	511.0 mL/g VS	

268

269

### 270 2.3. *Pyrolysis*

271 Pyrolysis is a process by which some solid wastes e.g. biomass can be decomposed in the  
272 absence of O<sub>2</sub>. Generally, gas, liquid and solid products are generated in pyrolysis process;  
273 however, the proportions of each phase depend on the operating conditions. Process  
274 temperature, residence time and vapor residence time are the key factors that can affect the  
275 proportions of the final products in each phase in this process. In general, high temperature  
276 along with long residence time are more appropriate for the purpose of gas production, while  
277 short residence time of vapor and mild temperature are suitable for producing liquid products.  
278 Furthermore, long vapor residence time coupled with low temperature are more appropriate in  
279 order to produce charcoals as the end product [61]. There are three subcategories of pyrolysis,  
280 i.e. fast, mild and slow pyrolysis [61-63]. Pyrolysis has been used for several centuries for the  
281 production of charcoal; however, the fast pyrolysis has attracted more attention in the recent  
282 decades because of interesting properties such as running the process at a relatively mild  
283 temperature of approximately 500 °C and with a short residence time of less than 2 s [61]. It is  
284 noteworthy that the fast pyrolysis is more appropriate for liquid production than the gas and  
285 solid phases production. Furthermore, tar and char are unfavorable products in pyrolysis  
286 process reacting with gaseous molecules, decreasing gas production and producing undesirable  
287 products. Therefore, these are considered as some of the challenges in hydrogen production  
288 during pyrolysis process [63]. The effects of some important factors such as moisture, density  
289 and composition of the materials pyrolyzed affecting more H<sub>2</sub> production will be discussed  
290 below [62].

291 The composition of the materials used in pyrolysis has demonstrated a considerable  
292 influence on H<sub>2</sub> production yield. Biomass, which is considered as one of the most appropriate  
293 materials for H<sub>2</sub> production by pyrolysis, is mostly composed of lignin, cellulose and  
294 hemicellulose, among which the higher the lignin content, the higher the proportion of H<sub>2</sub>

295 production. Lignin has a high thermal stability in a temperature range from 150 to 900 °C,  
296 which can be the reason for high capability of lignin for H<sub>2</sub> production. The density of the  
297 waste materials used is another factor affecting the proportion of H<sub>2</sub> generated by pyrolysis. As  
298 the materials with a lower density have less falling velocity in a reactor, there is more time to  
299 crack the hydrocarbons (HCs) and generate more H<sub>2</sub>. Moisture content of the materials  
300 pyrolyzed influences the decomposition rate of the materials and the types of final products  
301 over pyrolysis process. Generally, the more excessive the moisture content, the higher energy  
302 consumption and lower efficiency of the process. Therefore, it has been estimated that a 7%  
303 moisture content in pyrolyzed materials is regarded as a suitable proportion for all pyrolysis  
304 processes [62]. Furthermore, to enhance the performance of the pyrolysis, this process is more  
305 widely studied in hybrid or combined mode. Table 5 presents the overall operating conditions  
306 as well as the proportion of H<sub>2</sub> production from wastes. In addition, modeling is another option  
307 investigating different aspects of this process to enhance the controllability, product yield and  
308 efficiency of this process. However, insufficient validation is known as the main challenge in  
309 this regard. Some of the applied models in this process are computational fluid dynamics  
310 (CFD), distributed activation energy model (DAEM) and artificial intelligence based models,  
311 e.g. artificial neural network (ANN) and adaptive network-based fuzzy inference system  
312 (ANFIS) [64]. The application of the new modeling procedures with higher capabilities is  
313 gaining attention as a new tool in renewable energy research. Moreover, the determination of  
314 the gas products in this process is regarded as another crucial research field by virtue of the  
315 harsh environment, in a way that design and application of more advanced sensors to detect the  
316 products and process condition over running the process has great importance [64].

317

#### 318 *2.4. Gasification*

319 Gasification is a thermochemical process by which different types of compounds, e.g. organic  
320 wastes can be converted into useful products like H<sub>2</sub> under O<sub>2</sub>-deficient condition [63]. There  
321 are two common gasification processes for H<sub>2</sub> production from organic substances including  
322 steam critical water gasification and steam gasification [63].

323 The steam critical water gasification usually happens in supercritical state of water (374  
324 °C and 22.1 MPa), in a way that the liquid and gas states of water are miscible under this  
325 condition, when supercritical water as an oxidant can react with organic matter (e.g. HCs)  
326 molecules and generate CO<sub>2</sub> and H<sub>2</sub>. Although this is regarded as an interesting process for  
327 potentially high H<sub>2</sub> production from organic matter, the need for higher moisture content of the  
328 organic matter along with higher final cost of the produced H<sub>2</sub> than that of direct methane  
329 reforming are some limitations of this process [63].

330 Based on the process temperature conditions, the supercritical water gasification is  
331 classified into aqueous phase reforming, near critical catalyzed gasification and supercritical  
332 water gasification running at 215-265 °C, 350-400 °C and > 375 °C, respectively. The main  
333 products from these three categories are H<sub>2</sub> and CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> and CO<sub>2</sub>, consecutively.  
334 Overall, this type of gasification process is running at lower temperatures (approximately 600  
335 °C) than the dry gasification at 800-1200 °C. As this type of process takes advantage of water  
336 as medium, it is considered as an appropriate process for the application of wet materials in  
337 gasification [65].

338 Regarding the steam gasification, it needs a medium for reactions that may be a mixture of  
339 subcritical steam, O<sub>2</sub> and air. The final products are tar, N<sub>2</sub>, HCs, CO<sub>2</sub>, H<sub>2</sub>O, CO and H<sub>2</sub> from  
340 air gasification, HC, CO<sub>2</sub>, CO and H<sub>2</sub> from O<sub>2</sub> gasification, and tar, light HC, CO<sub>2</sub>, CO, CH<sub>4</sub>  
341 and H<sub>2</sub> from steam gasification processes, respectively. The average H<sub>2</sub> contents in final  
342 products of these processes are 15%, 40% and 40%, and their operating temperatures are in

343 ranges of 900-1100 °C, 1000-1400 °C, and 700-1200 °C, respectively. From the cost point of  
344 view, the most expensive one is O<sub>2</sub> gasification followed by the steam and air gasification [63].

345 Recently, these processes are more often running as a hybrid process with various catalysts.  
346 Mass and heat transfer among the particles can be simply carried out in the presence of  
347 catalysts, which increase the process performances in H<sub>2</sub> production [63]. Agglomeration and  
348 carbon deposition are two of the most important challenges in more efficient applications of  
349 the catalysts in this process; therefore, the application of different new and advanced  
350 procedures in design and synthesis of the catalysts is one of the hot research topics in this field  
351 [66, 67]. Table 5 indicates the different operating conditions of the catalytic gasification  
352 processes as well as their H<sub>2</sub> production performances.

353

## 354 2.5. Plasma

355 Plasma is a collection of ions, free electrons, radicals and neutrals [68, 69]. In 1879, plasma  
356 was identified as the fourth state of matter by William Crookes, and systematically studied by  
357 Langmuir in 1929 [70, 71]. Adequate and continuous energy is needed to generate and sustain  
358 the plasma, as otherwise the plasma components will be converted into neutral components.  
359 From the aspect of temperature, plasma can be categorized into two classifications, i.e. non-  
360 thermal and hot plasma. In non-thermal plasma, there is a considerable difference between the  
361 temperatures of electrons, ions and neutral gas [70]. In a way that depending on the applied  
362 procedure for plasma formation and the background gas used, the temperature of the electrons  
363 in non-thermal plasma can be varied from 10,000 to 100,000 °C. Whilst the other components of  
364 the plasma will be at room temperature [72]. However in hot plasma (3727-19727 °C), the  
365 temperature of electrons is the same as other species of the plasma [70]. In addition, there are  
366 other classifications for plasma conducted by the plasma discharge procedures including  
367 microwave, radio frequency and direct current, and reactor configurations, i.e. plasma spout

368 bed reactor, plasma entrained bed reactor, plasma moving bed reactor and plasma fixed bed  
369 reactor [70]. There are many applications for plasma, such as environmental remediation [69],  
370 coating [73, 74], membrane synthesis industry [71, 75], sterilization and gasification [70].  
371 Plasma gasification uses external power to increase and retain the temperature of the  
372 background gas and plasma components. During this process, the organic substances are  
373 broken down into their components via the active species, and the final materials produced are  
374 ash, slug and syngas [76]. In this process, the mass and quality of the produced gas are affected  
375 by some operating parameters like steam stream plus reaction temperature, oxidant, plasma gas  
376 flow rate and residence time. Regarding the mentioned nature for this process, plasma  
377 gasification has a considerable flexibility in receiving a wide spectrum of wastes and release  
378 very small volume of pollutants, e.g. metals (mercury) and PM needing further treatment [77].  
379 In addition, great controllability as well as high reactive activity and high enthalpy value are  
380 other known merits of this process [78]. In order to enhance the performance of this process in  
381 different applications for H<sub>2</sub> production, the hybrid form of this process such as catalytic  
382 plasma and thermal plasma pyrolysis has been considered [76].

383

384 **Table 5.**

385 The operating conditions and performances of pyrolysis, gasification and plasma processes.

Process	Bio-waste	Catalyst	Temp. (°C)	H <sub>2</sub> production/biomass	Reference
Catalytic-pyrolysis	Municipal sludge	Dental waste-derived sodium zirconate	900	142 mL/g	[79]
Catalytic-pyrolysis	Algae (Spirulina)	Dental waste-derived sodium zirconate	900	205 mL/g	[79]
Catalytic-pyrolysis	Methylcellulose	Dental waste-derived sodium zirconate	900	197 mL/g	[79]
Catalytic pyrolysis	Olive pomace	Ni-OPC	700	320 mL/g	[80]
Catalytic pyrolysis	Biomass of water hyacinth	FeCl <sub>3</sub>	540	117 mL/g	[81]
Catalytic steam gasification	Palm oil wastes	Tri-metallic (nano-NiLaFe/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> )	800	441 mL/g	[82]
Catalytic gasification	MSW	CaO	750	278 mL/g	[83]
Catalytic gasification	Corn stalk	CaO	650	574 mL/g	[84]
Catalytic gasification	Rice straw	CaO	650	567 mL/g	[84]
Catalytic gasification	Wheat straw	CaO	650	581 mL/g	[84]
Catalytic gasification	Peanut shell	CaO	650	586 mL/g	[84]
Thermal plasma gasification	Paper mill waste (PMW)	Combined water gas shift and pressure swing adsorption	1400-1450	400 NmL/g	[26]

386

387 The hazardous, toxic and resistant wastes cannot be easily decomposed and converted into  
388 H<sub>2</sub> by biological processes; therefore, pyrolysis, gasification and plasma processes are more  
389 suitable for the treatment of such wastes and generate H<sub>2</sub> simultaneously. As observed in  
390 Table5, the gasification-based processes have shown better potential to produce more hydrogen  
391 followed by plasma and pyrolysis-based processes regardless of the operating conditions and  
392 type of the wastes used. As indicated in Table 5, the highest H<sub>2</sub> produced belongs to catalytic  
393 gasification of peanut shell with 586 mL H<sub>2</sub>/g biomass. However, one of the most important  
394 drawbacks is that during these processes, both valuable gas (i.e. H<sub>2</sub>) and harmful gases (e.g.  
395 CO<sub>2</sub>, CO) are produced. Therefore, additional separation or treatment procedures are required  
396 to recover H<sub>2</sub> while removing or detoxifying hazardous gases, which will inevitably involve  
397 additional energy and cost.

398

### 399 **3. Techno-economic analysis**

400 Currently, approximately 98% of the hydrogen gas is produced by the consumption of fossil  
401 fuels using methane gas reforming or coal gasification methods, with which the main  
402 challenges remain the same as fossil fuels such as unsustainability, GHG emissions and global  
403 warming. Therefore, there has been a major shift towards the production of biogases from  
404 renewable biomass sources [85], based on the principles and importance of life cycle analysis  
405 (LCA).

406 TEA is a methodology framework to analyze the technical and economic performance of  
407 a process, product or service. TEA is a study performed on any industrial process to assess its  
408 profitability [86]. This type of study is usually performed on new technologies that show great  
409 lab-scale performance and have potential for commercialization. TEA describes both the  
410 economic performance and environmental impacts of the process, in both short-term and long-  
411 term [87]. TEA is also used to analyze the profitability and GHG emissions of new methods



412 for the treatment of waste and wastewater that are biomass-based [88, 89]. In this way, bio-  
413 waste and relevant wastewater containing biomass materials have a great potential to produce  
414 hydrogen gas as a clean source of energy to both decrease the GHG emission and by-product  
415 wastes and enhance the economy of the relevant industry [86, 90, 91]. For this purpose, general  
416 economic and technical conditions of the hydrogen production from biomass sources were  
417 studied using both lab-scale data and simulation software. The obtained results about various  
418 hydrogen production processes from biomass-based sources revealed that the economic part of  
419 the TEA directly depended on the maturity of the technology, availability and cost of bio-waste  
420 or wastewater, the market demand for hydrogen, and the capital and operational costs of the  
421 process [92-94].

422 From techno-economic point of view, the optimum scenario is to increase the hydrogen  
423 gas productivity and to decrease both the capital and operational costs, which will increase the  
424 feasibility of commercial-scale hydrogen production from biomass waste and wastewater. The  
425 capital cost relates to the land requirement and facilities, and operational cost relates to the  
426 supplementation and transportation of the feedstock and other required materials [63, 95, 96].  
427 However, the development of the technology and the local condition play an important role in  
428 the determination of the both capital and operational costs. Therefore, it is not possible to make  
429 a general rule for all cases [86]. In this way, an optimum value is obtained using simulation  
430 software like ASPEN or Hysys, concerning the optimum size of the plant and annual return  
431 rate of the costs according to the local price of hydrogen, feedstock, transportation, and  
432 materials [86, 87].

433 The maturity of a technology and its development is one of the most important obstacles  
434 in the way of commercialization of biomass-based hydrogen production technology. While the  
435 Technology Readiness Level (TRL) for traditional methods is adequately high (TRL 8) to  
436 reduce the production cost, the biological or electrochemical process for biomass conversion

437 have TRL less than 5 that dramatically increases the production cost [95, 97-99]. Furthermore,  
438 high price of the biomass-based feedstock and relevant operating costs (e.g. transportation)  
439 increase the biogas production cost for these types of processes. These expenditures therefore  
440 cause the production cost of hydrogen using biomass materials to be in the range of 1.2-2.4  
441 US\$/kg, while natural gas reforming can produce hydrogen with cost of less than 0.8 US\$/kg  
442 [88, 100]. To move forward, different hydrogen production methods using waste as feedstock  
443 will need to conduct their individual economic analysis and LCA. In general, the production  
444 cost of hydrogen gas should be close to 0.3 US\$/kg H<sub>2</sub> which is equivalent to the price of  
445 gasoline (2.5 US\$/GJ), in order to increase the commercial favorability of a production process  
446 [101].

447

### 448 *3.1. Process economics*

449 The potential capacity of Turkey as a sample country for the production of biogas and hydrogen  
450 from wastewater of the milk-processing factory was investigated [72]. The results revealed that  
451 annually more than 50 million m<sup>3</sup> of biogas and about 13000 ton of hydrogen gas can be  
452 produced by the treatment of wastewater from milk-processing plants. In addition, the energy  
453 efficiency of the simulated plants can reach 70% and 48%, respectively and the energy saving  
454 of the processes can reach the value of 15 million US\$/yr [96].

455 The effective treatment of bio-waste such as agricultural waste, MSW and wastewater as  
456 well as the production of biogas are the first step of commercialization, and most efforts are  
457 performed in lab-scale to evaluate the efficiency of different methods. On the other hand, the  
458 process economy plays the dominating role in large-scale production; therefore, the lab scale  
459 results are coupled with simulation modelling to estimate both the production and economic  
460 efficiency of large-scale systems. In practice, the lab-scale results are used for the prediction  
461 of large scale systems using a simulation software e.g. ASPEN Plus [92].

462 The maturity of a technology and its development is one of the most important obstacles  
463 in the way of commercialization of biomass-based hydrogen production. TRL has been  
464 introduced to grade the maturity of technology for its readiness to commercialization. TRL is  
465 a number from 1-9, with higher TRL values demonstrating more well-developed technology  
466 which is closer to economic and cost-effective commercialization. The TRL commences with  
467 a value of 1 that shows the process is at basic technology research stage, then increases to  
468 higher values revealing research for evaluation of feasibility, development of technology,  
469 development of the system, and finally the operation test of the system, which is equal to TRL  
470 9 [4]. Although the simulated results provide a detailed view about the economic feasibility of  
471 the process, they cannot be used without constraints. In other words, the derived results are  
472 obtained according to the initial local economic and environmental conditions, which will vary  
473 between countries or even between different regions of the same country.

474 For example, Li et al. [102] have used dark fermentation process for the production of  
475 hydrogen from biomass. In their study, the hydrogen was produced from both wastewater and  
476 agricultural waste in lab scale and ASPEN Plus was used for estimation of large-scale  
477 production. Their results demonstrated that the maximum annual profit would be obtained by  
478 a working volume of 100 m<sup>3</sup> of wastewater and 400 m<sup>3</sup> of agricultural waste that respectively  
479 obtained annual return of 81% and 30%. It was estimated that on local price evaluation, the  
480 revenue of biogas production is approximately 2.7 million US\$/yr from the wastewater  
481 treatment and 2 million US\$/yr from the treatment of agricultural waste. Such economic  
482 analysis shows a high feasibility of commercialization for hydrogen production from  
483 agricultural wastes and wastewater.

484 In other studies, the economic efficiency of various biomass-based plants for the  
485 production of hydrogen gas was estimated. The production cost of H<sub>2</sub> biogas in different  
486 processes is directly dependent on the facilities used for treatment process as well as the

487 efficiency of the process. Therefore, from a commercial point of view, both the production  
488 efficiency and instalment and operational cost should be fully considered. For example, the  
489 electrolysis system can be used for hydrogen production with a conversion efficiency of about  
490 50%, as a result, the hydrogen production cost is 10 US\$/kg, which is much higher than  
491 gasification process [103]. The economic evaluation performed on different gasification  
492 process showed that the average hydrogen production cost is about 1.7-2.2 US\$/kg [93, 104].  
493 However, the efficiency of the gasification process depends on the method used. This process  
494 can produce up to 190 g H<sub>2</sub>/kg of agricultural waste [94, 105]. In a study, the fluidized bed  
495 (FB) gasification process could produce cheaper hydrogen gas compared to entrained flow (EF)  
496 gasification, but the thermal efficiency of the EF is much higher than FB [89].

497 Beside the favorable results of both FB and EF gasification processes, the high price of  
498 biomass is the main obstacle for commercialization. The financial analysis shows that the  
499 biomass price should be less than 60 US\$/ton in order to produce hydrogen at a price which  
500 can cover the cost of the process. However, gasification process with carbon capture can be  
501 followed to simultaneously produce and sell CO<sub>2</sub> that can compensate for the higher price of  
502 the biomass feedstock [89].

503 In general, the gasification process is the most commercialized method for hydrogen  
504 production. In this method, the average thermal efficiency of the hydrogen is about 50%, which  
505 is in the moderate range. Furthermore, the levelized cost of hydrogen (LCOH) production from  
506 biomass sources is in a wide range of 1.4-5.2 US\$/kg, which highly depends on the scale of the  
507 system and the biomass waste cost. Salkuyeh et al. [80] investigated the effect of cost of  
508 biomass on the final cost of hydrogen, and identified the high dependency of the economy of  
509 the gasification process on the biomass waste cost, in which the hydrogen gas cost can be as  
510 low as 0.5 US\$/kg when using zero-cost feedstock to about 4.5 US\$/kg [89]. Therefore, the  
511 installation of hydrogen production plant in the vicinity of agricultural processing plants that

512 produce large quantities of biomass waste can bring major values to the processing plant.  
513 Furthermore, the calorific values of the wastes are different which have a major impact on the  
514 plant production efficiency and on the economy and environmental behavior of the process.  
515 The pre-treatment process like separation of hazardous materials from feedstock is also an  
516 important step of gasification that comprise a potential significant part of the operational cost  
517 of project. In addition, securing long-term local supply for feedstock wastes and customers for  
518 produced biogases is another important challenge in the overall appraisal of biogas production  
519 process [33, 106].

520 Additionally, different studies showed that the capital cost of the gasification process is in  
521 the range of 10-20% of total cost [33]. Although the TRL for gasification process is among the  
522 highest and showed adequate maturity in technology development of the process, it still suffers  
523 from immaturity of technology for waste pre-treatment. Additionally, the market demand for  
524 produced hydrogen is still developing, which may hinder the commercialization of hydrogen  
525 production technologies.

526 In most cases, a single method cannot provide sufficient gas production efficiency to  
527 compensate for its cost and therefore combined methods are used to take advantage of more  
528 than one method and decrease the hydrogen gas production. Although fermentation process  
529 showed suitable capability for agriculture waste and wastewater treatment, different treatment  
530 methods follow separate process and generate different process efficiency. In this way, some  
531 techno-economic studies were performed to investigate the H<sub>2</sub> production efficiency.  
532 Furthermore, it is possible to combine fermentation methods in a single process to increase the  
533 production efficiency. Han et al. [83] studied the efficiency of a combined system of both SSF  
534 and dark fermentation for the production of hydrogen gas from a plant having the treatment  
535 capacity of 10 ton/d of food waste. The results show that the annual return rate of plant is more  
536 than 20% and the hydrogen production cost is 2.3 US\$/m<sup>3</sup>, which is 0.4 US\$/m<sup>3</sup> cheaper than

537 market price of H<sub>2</sub> [107]. The study has proven the feasibility of the fermentation process for  
538 biogas production.

539 In another study, a combination of dark fermentation and photo fermentation was used to  
540 produce hydrogen gas from sugar factory waste and to evaluate the effectiveness of the  
541 combined system. The wide availability of sucrose-based waste (e.g. molasses) which  
542 decreases the cost of feedstock, and high content of amino acids and other organic materials  
543 that prepare grounds for rapid growth of microorganisms increase the favorability of this type  
544 of biomass wastes for hydrogen generation. However, a computer-based analysis of this  
545 combination of processes showed it to be unfavorable from economic point of view due to the  
546 high cost of photo fermentation stage [108]. Additionally, some other studies revealed that the  
547 H<sub>2</sub> production cost in fermentation processes highly depends on the photo fermentation, due to  
548 low productivity of this step that increases the needs of high volume of fermentor and large  
549 space requirements. In addition, the conversion efficiency of the photo fermentation process is  
550 less than 5%. The most significant part of this cost is due to the cost of plastic tubing for the  
551 photo fermenters that contribute more than one third of hydrogen production cost [109].  
552 Additionally, as acids are produced during the fermentation process, and the hydrogen  
553 productivity of the process is dependent on the pH that needs accurate adjusting and control,  
554 thereby increasing the overall cost of the process.

555 MEC is an exciting hydrogen production process due to dramatic decrease in its electrical  
556 consumption, and no need for pre-treatment or purification, therefore increasing its economic  
557 competitiveness. On the other hand, the high cost of catalyst, high susceptibility to CO  
558 poisoning, and low hydrogen production (~70 g/kg of feedstock) were its disadvantages [110].  
559 The anode and collector materials comprise 94% of the total material costs of MEC, which  
560 accounts for significant part of the process [111]. A lab-scale MEC was used for the production  
561 of hydrogen from renewable sources, and hydrogen production rate of 120 mL/L.d was

562 achieved, although its economy is not so optimistic [112]. The lab-scale results suggested that  
563 by the development of technology towards higher TRL, the MEC process could generate better  
564 large-scale performance.

565 Pyrolysis is another straightforward method for the treatment of agricultural waste and  
566 production of hydrogen. The pyrolysis process is relatively simple, can be performed in large-  
567 scale, and possess a high TRL 7, which will decrease its capital costs. However, the high  
568 emissions of GHG like CO<sub>2</sub> caused LCA challenges for this method. In the lab-scale system,  
569 the hydrogen production rate of the process was 65 g per kg of rice husk biomass and purity of  
570 60% was achieved that shows moderate-to-high quality of this process for commercialization.  
571 In the pyrolysis process, the hydrogen yield and tar residue consumption were increased by  
572 increasing the temperature that increase the operational cost of the process as well [63]. In  
573 another study, the fast pyrolysis method was used to model the process of hydrogen production  
574 from corn waste and results demonstrated that the production cost of hydrogen was 2.1-3.1  
575 US\$ per kg of hydrogen. The simulation results also revealed the high dependency of the  
576 process cost on the price of biomass feedstock [90, 91].

577 Plasma gasification is a new generation of methods for the production of hydrogen gas.  
578 The most economical advantage of the plasma gasification is its complete conversion of carbon  
579 materials with no organic waste residues. The application of plasma is more dominant in a  
580 catalytic reaction process, because plasma can convert all materials that may have poisonous  
581 effect on the catalyst and bypass the pre-treatment step. This process can be cost effective for  
582 the production of biogas. However, due to the high operation cost from its high electrical power  
583 consumption, this method is very expensive for the treatment of high volume of agricultural  
584 waste and is mainly used for the gasification of special types of wastes like printed circuit  
585 boards, medical wastes, or metallurgical wastes. The power consumption of this method may  
586 reach more than 20% of the costs of the plant [33]. In a study, plasma was used in gasification

587 process in small-scale system and the hydrogen cost was 2.4 US\$/kg, which is comparable with  
588 commercial gasoline. The results show high potential of plasma for special waste treatment  
589 application to produce hydrogen gas [113]. Table 6 summarizes the produced H<sub>2</sub> cost, and  
590 TRLs of the reviewed processes for commercial situation of all these processes.

591 As observed in Table 6, the gasification process has been commercialized and the cost of  
592 produced H<sub>2</sub> by this process is lower than the others. From the aspect of less H<sub>2</sub> price, there is  
593 almost same condition for dark, solid state and with roughly 2.3 US\$/kg followed by plasma  
594 with 2.4 US\$/kg, pyrolysis with approximately 2.6 US\$/kg, MEC and photo-fermentation with  
595 around 2.8 and 3.5 US\$/kg consecutively. From the TRL point of view, gasification process  
596 with TRL 9 has ranked the first followed by pyrolysis, dark fermentation, SSF, photo-  
597 fermentation, plasma and MEC in decreasing order.

598

#### 599 **4. Life cycle analysis**

600 LCA is considered as a beneficial procedure to detect the environmental hotspots and  
601 demonstrate the possible emissions during a process, therefore appropriate solutions can be  
602 brought up to minimize the undesirable environmental effects [114]. A standard LCA  
603 procedure is conducted based on the ISO 14040 and ISO 14044, according which there are four  
604 stages, i.e. goal and scope definition, life cycle inventory, LCA and interpretation [115].

605

606

607



608 Table 6. The economic, commercialization, and technology readiness level of H<sub>2</sub> production processes from biomass

Process	H <sub>2</sub> production cost (US\$/kg)	Commercial scale	Hydrogen production (g H <sub>2</sub> /kg biomass)	TRL	Reference
Fluidized bed gasification	2.1	Small scale	-	9	[88, 100]
Plasma	2.4	Lab-scale	-	4	[33, 113]
Gasification	1.7–2.2	Large scale	50-180	9	[63, 89, 107]
Natural gas reforming	0.8	Large scale	35-110	9	[100]
Gasoline price	0.3	Large scale	-	9	[101]
Electrolysis	3.5- 10	Lab scale	20-85	4	[103]
Dark fermentation	2.3	Pilot scale	8-45	5	[102, 107, 116]
Photo fermentation	3.5	Lab-scale	9-45	4	[117, 118]
SSF	2.29	Lab-scale	15-32	5	[119, 120]
Pyrolysis	2.1-3.1	Medium scale	25-55	7	[90, 91]
MEC	1.1-4.5	Lab scale	70	2-4	[121, 122]

609

610 In the first stage, the purpose of the LCA in H<sub>2</sub> production systems is the quantification and  
611 detection of the emissions to the abiotic and biotic environments during all steps of the process.  
612 In addition, the assessment of the environmental impacts of the required energy and materials  
613 during H<sub>2</sub> production and utilization processes along with giving appropriate solutions to  
614 decrease these detrimental effects are taken into account as another general purpose of this  
615 stage. In second stage, all inputs and outputs of the defined boundaries are quantified and  
616 compiled [115]. In third stage, the outcomes of the second stage are classified into different  
617 impact classifications, e.g. human toxicity through soil, through water and through air along  
618 with some indexes like global warming potential, ozone depletion, water consumption and  
619 resource consumption. Then, indicators which have been defined in scientific documents are  
620 used to estimate the potential impact of each item such as different resource usages and each  
621 emission. In fourth stage, the outcomes of the first three stages are reviewed, argued and  
622 interpreted. During this stage, the appropriate solutions to decrease the detrimental effects are  
623 recommended [115]. LCA of different biogas production systems have been analyzed to  
624 address their environmental characteristics. However, since there are some limited and sporadic  
625 studies for LCA assessment of hydrogen production processes from organic waste, the related  
626 and comparable studies were listed in Table 7 and discussed below.

627 The comparison of different studies revealed that production of hydrogen gas from biomass  
628 sources could decrease the GHG emission. The biomass-based plant can produce up to 75%  
629 lower GHG compare to natural gas reforming process. In this way, gasification process showed  
630 dramatically lower CO<sub>2</sub> emission and fossil fuel demand compare to reforming processes [20].

631 For study of the cradle-to-grave LCA, it is mandatory to cover the impact of different  
632 parameters include raw material production, pre-treatment, collection, transportation, biogas  
633 production process, and hydrogen purification, transportation and application [123]. The  
634 comparison of different studies showed better LCA of biomass to hydrogen processes, compare  
635 to production of hydrogen form coal. The results showed that in process of production of

636 hydrogen, life cycle energy consumption of biomass-based process is about one-fourth of coal-  
637 based process. Furthermore, about 90% less GHG were emitted by using biomass materials. In  
638 addition, pipeline is most environmentally friendly method for the transportation of produced  
639 hydrogen and has less GHG emission [124].

640 Although the economic competitiveness of hydrogen production from biomass material is  
641 still to be improved, its environmental friendliness and low GHG emission increase the  
642 motivation to increase the maturity of such technology towards commercialization. More than  
643 98% reduction of GHG emission by using biomass material has shown great long-term positive  
644 impact on mitigating global warming [125]. However, the source of biomass makes a big impact  
645 on LCA of the process. Using biomass resources that produce a high yield of H<sub>2</sub> gas, such as  
646 eucalyptus, will improve the economics and LCA result [126].

647 From environmental point of view, LCA of plasma gasification was performed in some  
648 studies and results showed that plasma gasification has better saving in the energy and material  
649 resources. Furthermore, the amount of GHG emission, freshwater and air pollution was lower  
650 compare to incineration, and higher amount of energy was produced. Overall, plasma  
651 gasification showed negative values for all investigated environmental categories, which reveal  
652 higher environmental advantageous [127].

653 On the other hand, LCA was performed to compare two gasification processes, i.e. fluidized  
654 bed (FB) gasification and entrained flow (EF) gasification. The results showed that the life  
655 cycle energy of the EF system is 20% less than the FB system, which demonstrates a better  
656 environmental performance of EF system [89].

657 **Table 7.**

658 The life cycle assessment of the H<sub>2</sub> production processes from biomass.

Process	Bio-waste	Final fuel products	Net GHG emissions	Reference
Fermentation	Food waste; microalgae	CH <sub>4</sub> , H <sub>2</sub>	15.1 kg CO <sub>2</sub> -eq/kg H <sub>2</sub>	[128]
MEC	Urban wastewater	H <sub>2</sub>	18.8 kg CO <sub>2</sub> -eq/kg H <sub>2</sub>	[114]
Gasification	Coal	H <sub>2</sub>	18.0 kg CO <sub>2</sub> -eq/kg H <sub>2</sub>	[114]
Plasma Gasification	MSW		31 kg CO <sub>2</sub> -eq/kg MSW	[127]

659

660 According to the results reported in Table 7, the dark fermentation process generates the lowest  
 661 production of 15.12 kg CO<sub>2</sub>-eq/kg hydrogen, and is therefore the best process among the  
 662 gasification, plasma and MEC, on the basis of GHG emissions. It is worth highlighting that  
 663 Rosen [129] has highlighted the importance of the advanced sustainability assessment tools  
 664 such as exergy and its combinations with LCA and economic analysis, i.e.,  
 665 exergoenvironmental and exergoeconomic analyses in biofuel industries which can be applied  
 666 for investigation the sustainability features of various H<sub>2</sub> production platforms as well;  
 667 however, there is a big knowledge gap in this regard which can be taken into more consideration  
 668 in this field. In addition, Soltanian *et al.* [130] critically reviewed the exergetic aspects of  
 669 lignocellulosic biofuels suggested the exergoenvironmental and exergoeconomic procedures as  
 670 two more comprehensive and advanced tools to analyze such systems and make a right decision.

671

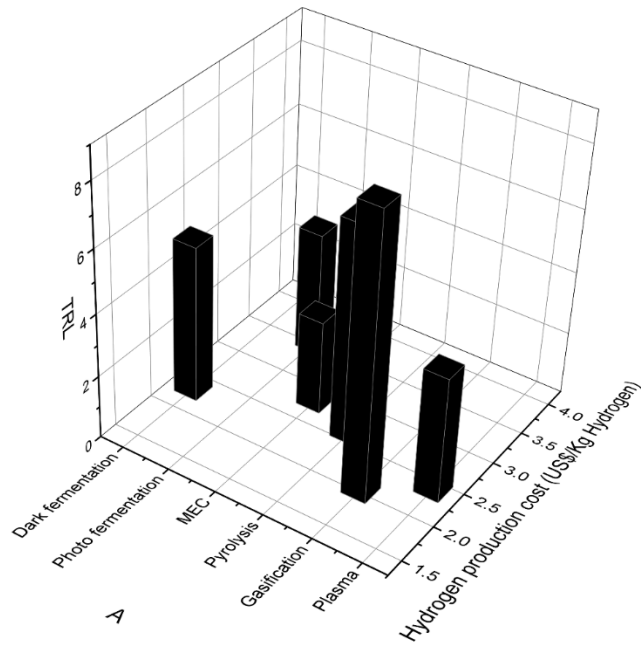
672 **5. Process comparison for efficiency, economics and environmental impacts**

673 In order to prioritize different processes to apply for H<sub>2</sub> production from organic wastes, there  
 674 is a strong need to compare the capabilities of the processes from aspects of efficiency,  
 675 economics and environmental footprint. Therefore, regarding the presented information in  
 676 Tables 2-5, the average values of H<sub>2</sub> production by different single and combined processes  
 677 were calculated and presented in Fig. 2. For economic comparison, the average cost of the H<sub>2</sub>

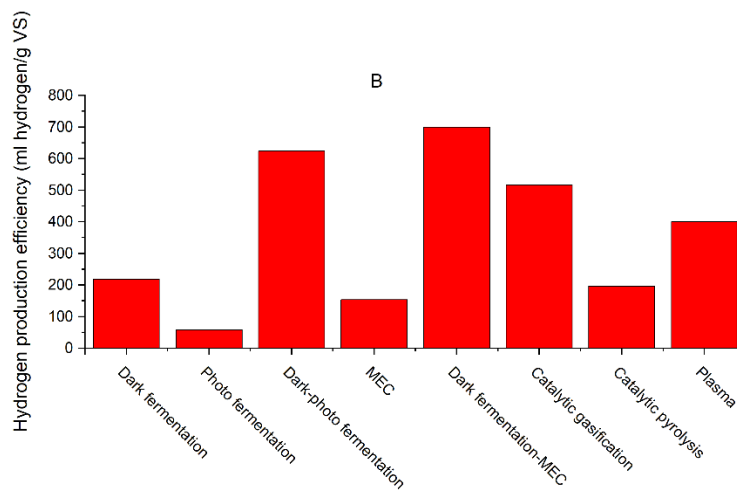
678 produced is shown in Table 6 and the TRL of the processes are demonstrated in Fig. 2. Although  
 679 there is lack of environmental assessment information for all the processes studied, using the  
 680 information listed in Table 7, the GHG emission potential from different processes is shown in  
 681 Fig. 2 for comparison.

682

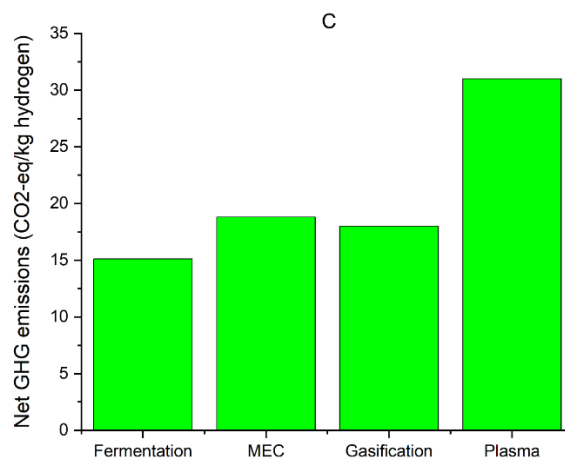
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686

687 **Fig. 2.** Comparison of different H<sub>2</sub> producing processes from bio-waste for (A) cost and TRL,  
 688 (B) efficiency, and (C) net GHG emission.

689 As observed in Fig. 2B, regarding the H<sub>2</sub> production efficiency, the combined dark  
 690 fermentation-MEC process was the best process, followed by the combined dark-photo  
 691 fermentation, catalytic gasification, plasma, dark fermentation, catalytic pyrolysis, MEC and  
 692 photo fermentation respectively. From the aspect of the TRL, the gasification process ranked  
 693 first followed by pyrolysis, dark fermentation, photo-fermentation, plasma and MEC  
 694 respectively. Regarding the cost of H<sub>2</sub> produced, the cheapest process is gasification followed  
 695 by dark fermentation, plasma, pyrolysis, MEC, and photo fermentation correspondingly. From  
 696 the GHG emission assessment, the fermentation process was the best, followed by gasification  
 697 process, MEC process, with plasma process being the worst.

698

## 699 **6. Practical implications**

700 The results of the present work underline the capabilities and limitations of the potential H<sub>2</sub>  
 701 production processes from bio-wastes/wastewaters. In addition, the research trends of these  
 702 processes are suggested. The selection of an appropriate process for H<sub>2</sub> production from bio-  
 703 wastes is the first step in the decision making, this study will help the engineers and researchers  
 704 to compare and choose the best one based on the capabilities and limitations of each process.  
 705 Based on the initial appraisal, further research may be needed for verification before full  
 706 commercial operations. Moreover, the findings from this study should support the engineers

707 and researchers to focus on the bottlenecks of the selected processes for further research and  
708 problem solving.

709

## 710 **7. Conclusions and future research perspectives**

711 To address the increasing global energy demand and environmental challenges, hydrogen  
712 production from bio-wastes has gained significant attention. There are several processes for H<sub>2</sub>  
713 production from bio-waste such as dark, photo and solid-state fermentation, MEC, pyrolysis,  
714 gasification and plasma. This work critically reviewed the capability, limitation and commercial  
715 potential of these different processes based on techno-economic and environmental impact  
716 analysis. Based on capabilities of the processes for H<sub>2</sub> production, the dark fermentation process  
717 showed higher performance than others. Most of the hybrid or combined processes  
718 demonstrated great performance in H<sub>2</sub> production from bio-waste, including dark fermentation-  
719 MEC, dark-photo fermentation, catalytic pyrolysis, and catalytic gasification. Regarding the  
720 production cost, the cheapest H<sub>2</sub> production belonged to gasification at 2 US\$/kg and dark-  
721 fermentation at 2.3 US\$/kg, followed by plasma, pyrolysis, MEC and photo-fermentation.  
722 Based on LCA, fermentation produced the lowest GHG emissions followed by gasification,  
723 MEC and plasma processes. However, there are still many deficiencies regarding the  
724 technological, economic and environmental performances of these processes. Future research  
725 should focus on improving the hydrogen production efficiency of the hybrid and combined  
726 processes so as to increase their TRL value and reduce the overall cost. Furthermore, the techno-  
727 economic and environmental impact assessments are needed especially for emerging hybrid  
728 technologies with low TRL, in order to support their transition and adoption in the energy  
729 industry. In addition, investigating the sustainability features of the various H<sub>2</sub> production  
730 systems through exergoenvironmental and exergoeconomic procedures as two advanced  
731 sustainability assessment tools is expected to become future research priority.

732

733

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738

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