

Journal Pre-proofs

Review

Lignocellulose biohydrogen towards net zero emission: A review on recent developments

Chyi–How Lay, Jeyaprakash Dharmaraja, Sutha Shobana, Sundaram Arvindnarayan, Retnam Krishna Priya, Rajesh Banu J, Rijuta Saratlae, Young Kwon Park, Vinod Kumar, Gopalakrishnan Kumar

PII: S0960-8524(22)01417-1
DOI: <https://doi.org/10.1016/j.biortech.2022.128084>
Reference: BITE 128084

To appear in: *Bioresource Technology*

Received Date: 3 September 2022
Revised Date: 2 October 2022
Accepted Date: 4 October 2022

Please cite this article as: Lay, C., Dharmaraja, J., Shobana, S., Arvindnarayan, S., Krishna Priya, R., Banu J, R., Saratlae, R., Kwon Park, Y., Kumar, V., Kumar, G., Lignocellulose biohydrogen towards net zero emission: A review on recent developments, *Bioresource Technology* (2022), doi: <https://doi.org/10.1016/j.biortech.2022.128084>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2022 Elsevier Ltd. All rights reserved.



1 **Lignocellulose biohydrogen towards net zero emission: A review on recent developments**

2 Chyi–How Lay^{1,#}, Jeyaprakash Dharmaraja^{2,#}, Sutha Shobana³, Sundaram Arvindnarayan⁴,
3 Retnam Krishna Priya⁵, Rajesh Banu J⁶, Rijuta Saratlae⁷, Young Kwon Park⁸, Vinod Kumar⁹,
4 Gopalakrishnan Kumar^{10*}

5

6 ¹ Department of Environmental Engineering, Feng Chia University, Taichung, Taiwan

7 ² Division of Chemistry, Faculty of Science and Humanities, AAA College of Engineering and
8 Technology, Amathur–626005, Virudhunagar District, Tamil Nadu, India.

9 ³ Green Technology and Sustainable Development in Construction Research Group, Van Lang
10 School of Engineering and Technology, Van Lang University, Ho Chi Minh City, Vietnam.

11 ⁴Department of Mechanical Engineering, Lord Jegannath College of Engineering and
12 Technology, Marungoor – 629402, Kanyakumari District, Tamil Nadu, India.

13 ⁵Research Department of Physics, Holy Cross College (Autonomous), Nagercoil – 629004,
14 Kanyakumari District, Tamil Nadu, India.

15 ⁶Department of Life Science, Central University of Tamilnadu, India

16 ⁷Research Institute of Integrative Life Sciences, Dongguk University–Seoul, Ilsandong–gu,
17 Goyang–si, Gyeonggi-do, 10326, Republic of Korea

18 ⁸School of Environmental Engineering, University of Seoul, Seoul 02504, Republic of Korea

19 ⁹School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, United
20 Kingdom

21 ¹⁰School of Civil and Environmental Engineering, Yonsei University, Seoul 03722, Republic of
22 Korea,

23

24 # Authors have equal contribution to this work.

25

26

27 ***Corresponding Author:**

28 Gopalakrishnan Kumar, Email: gopalakrishnanchml@gmail.com

29

31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62

Abstract

This review mainly determines novel and advance physical, chemical, physico-chemical, microbiological and nanotechnology-based pretreatment techniques in lignocellulosic biomass pretreatment for bio-H₂ production. Further, aim of this review is to gain the knowledge on the lignocellulosic biomass pretreatment and its priority on the efficacy of bio-H₂ and positive findings. The influence of various pretreatment techniques on the structure of lignocellulosic biomass have presented with the pros and cons, especially about the cellulose digestibility and the interference by generation of inhibitory compounds in the bio-enzymatic technique as such compounds is toxic. The result implies that the stepwise pretreatment technique only can ensure eventually the lignocellulosic biomass materials fermentation to yield bio-H₂. Though, the mentioned pretreatment steps are still a challenge to procure cost-effective large-scale conversion of lignocellulosic biomass into fermentable sugars along with low inhibitory concentration.

Keywords: *Lignocellulosic biomass; bio-H₂; Pretreatment; Nanotechnology; Challenges.*

63 1. Introduction

64 The lignocelluloses have been originated from both the edible and non-edible industries
65 and are sustainable as well as promising materials for the productivity of second generation bio-
66 fuels, which mainly include bio-ethanol, bio-H₂, biogas, bio-methane, synthetic bio-fuels, bio-
67 diesel *etc.* Lignocellulosic biomass is a renewable resource and an interesting alternative for
68 fossil fuels since it consists of large amounts of energy as well as organic compounds. Further,
69 lignocelluloses are a basic components of plant materials and has widely been utilized by
70 biorefinery, cosmetic, food and pharmaceutical industries, as well (Ashokkumar et al., 2022;
71 Kumar et al., 2019; Ponnusamy et al., 2019). In the way, such materials obtained from flowers,
72 energetic willow, grasses, miscanthus, poplar trees, and stems, are functioning as fillers in the
73 fabrication of beauty masks, curative chows and thermoplastic composite materials. Some other
74 significant sources of the lignocellulosic biomass materials are the residual forms procured from
75 agricultural wastes, cereal, corn straw, corncob, forest, paper industry, potato haulms, rapeseed
76 oil pressing, sawmills, sugar beets, sunflowers, waste paper industries and other waste fragments
77 of plants as well as firewood (Azbar et al., 2009). The biomass structure only defines the kind of
78 pretreatment techniques, required. The bio-H₂ that is procured from lignocelluloses *via*
79 fermentation is an alternative to petro-derived fuel itself as it is eco-friendly since there is no
80 emission of GHGs (greenhouse gases), mainly CO₂ (carbon dioxide) while its combustion
81 (Moreno and Dufour, 2013). Further, bio-H₂ is a basic molecule in a range of chemicals as well
82 as petro-chemical processes, like production of ammonia, integrated circuits and optical fibers,
83 methanol, methane, nitrobenzene derived aniline from nitrobenzene, polymers syn-gas,
84 hydrogenation derived olefins, *etc.* Bio-H₂ is also used in the petro-chemical processes of
85 hydro-amination, hydro-cracking and hydro-conversion (Gómez et al., 2011). Beyond from the
86 lignocellulosic bio-energy source, the bio-H₂ can crucially be generated with energetic
87 potentiality by means of gasification from coal & coke, reforming process of steam methane as
88 well as water gas from crude oil derived hydrocarbons, electrolysis of water and water gas shift.
89 All such processes not only need a high input of electrical power and fossil fuels utilization but
90 also depletion of green environment by means of air pollution. So, bio-resources have been
91 considered for larger scale production of bio-H₂ (Goryunov et al., 2016). In such a way the
92 biomasses can be an alternative option to produce sustainable bio-H₂ energy to achieve short-

93 term emission reductions (Balat, 2011). In the Europe, about 67% of preliminary energy has
94 been procured primarily from biomass renewable resources with nearly about 14–19 MJ/kg
95 calorific value and further the produced total bio–energy electricity is about 370 TWh, initially
96 from the year of 2012. According to IEA (International Energy Academy), it occupies absolutely
97 1.5% of the generation of world electricity (Sun and Cheng, 2002). The lingo–cellulosic
98 materials biorefinery yield nearly 48 % of the biomass–derived energy under favorable
99 circumstances (Sun and Cheng, 2002). The main by–products of bio–refineries apart from the
100 bio–H₂ are the biomaterials and certain bio–chemicals *viz.* bio–ethanol and furan are very
101 important for environmental energy security as it possesses socio–economic advantages
102 associated with biodiversity, food security, reduction of greenhouse gases emission, and
103 sustainable bio–energy development (Balat, 2011; Sun and Cheng, 2002). The generation of
104 energy/power forecasts that the produced energy has been raised from 200 TWh by the year of
105 2006 to 380 TWh by the year of 2016, globally and it has reached 600 TWh in 2020 (IEA, 2015).
106 The limitation of lignocellulosic derived bio–H₂ *via* fermentation is the formation sugar
107 intermediates during hydrolysis. Thereby, it requires a proper lignocellulosic pretreatment in
108 bio–H₂ productivity. The aim of the pretreatment technique includes change in the rigid
109 lignocellulosic by means of digestion to increase the accessibility of a range of hydrolytic
110 reagents/factors like suitable chemicals, enzymes, *etc.*, for the decomposition of organic matters.
111 These can be metabolized by fermentation process with the support of microorganisms. The
112 lignocellulosic biomass derived bio–H₂ production necessitates the development in commercially
113 and eco–friendly technologies towards the pretreatment process (Hendriks and Zeeman, 2009).
114 In this concern, the lignocellulosic biomass pretreatment techniques on its structure have
115 highlighted herein with the pros and cons of each technique, especially about the cellulose
116 digestibility. This review mainly focuses on novel and advances physical, chemical, physico–
117 chemical, microbiological and nanotechnology based pretreatment techniques towards
118 lignocellulosic biomass pretreatment for bio–H₂ production *via* fermentation.

119

120 2. Lignocelluloses and pretreatments

121 The lignocellulosic biomass recalcitrance is mainly depend upon the complex plant cell
122 wall, heterogeneous crystalline cellular components, and the extent of lignification, further these

123 are all the key facts to make the cell resistant/accessible to chemical and bio reagents. Thereby,
124 the recalcitrance of lignocellulosic biomass materials has been done eventually by means of the
125 pretreatment techniques as they hold a prominent role in the utilization of those biomass
126 materials towards industrial applications. Before the downstream process of disintegration of
127 complex lignin structure, using the suitable pretreatment techniques can be employed for
128 reducing the crystallinity and solubilization of hemicellulose content. Thereby, the accessibility
129 of reagents/enzymes and enhancement of their activity over the surface has been increased
130 towards the lignocellulosic biomass materials (Abraham et al., 2020). The suitable pretreatment
131 mainly offers the digestion of cellulose, hemicellulose and lignin moieties of lignocellulosic
132 materials, consequently followed by reduction in size of the lignocellulosic particles. Thus, there
133 is a way to enrich the available surface areas for efficient reagent/enzymatic processes, which
134 can obviously lead to effective conversion /degradation / digestibility of the complex
135 polysaccharides of the lignocellulosic materials into simple monomers and are easily
136 metabolizable / easily producing fermentable sugars to yield bio-H₂. There is further conversion
137 of valuable bio-H₂ while the hydrolytic process with low energy consumption, accompanied by
138 the formation of non-toxic enzyme inhibitors, *etc* (Abraham et al., 2020; Dharmaraja et al.,
139 2019; Mankar et al., 2021; Usmani et al., 2020). Recently, various pretreatment techniques have
140 been employed for dissimilar lignocellulosic materials and each technique possesses its own pros
141 and cons. There are five kinds of pretreatment techniques (Fig. 1) viz. (i) physical, (ii) chemical,
142 (iii) physico-chemical / thermo-chemical (iv) biological and (v) nanotechnology based
143 pretreatment techniques (Anu et al., 2020; Ashokkumar et al., 2022; Dharmaraja et al., 2019;
144 Kucharska et al., 2018; Singh et al., 2018), which all are widely been employed for the
145 lignocellulosic materials pretreatment processes. Each technique follows its own characteristic
146 experimental conditions to break the complex structure of lignocellulose materials to yield bio-
147 H₂ and a range of value added products, besides.

148

149

150

151

152

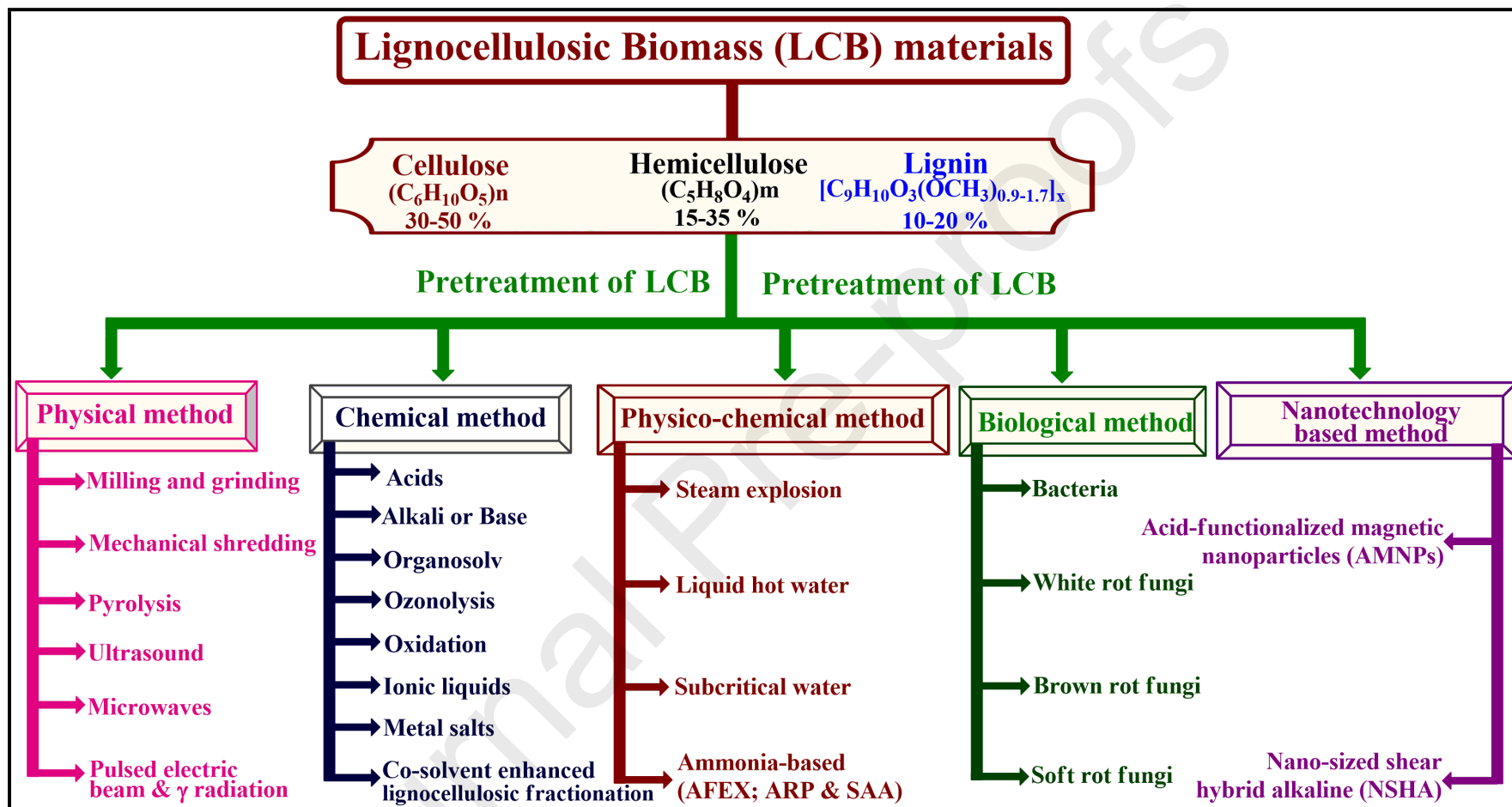


Fig. 1. Various pretreatment methods for lignocellulosic biomass materials.

157 **3.1. Lignocellulosic pretreatment by physical methods**

158

159 The pretreatment by physical processes strongly enhances the hydrolytic efficacy and
160 the decomposition of biomass anaerobically not only to liquid as well as gaseous bio-fuels
161 but also some other value added bio-products (Chandel et al., 2022; Sinha and Pandey,
162 2011). Abbasi and Abbasi (Abbasi and Abbasi, 2010), has shown the bio-H₂ productivity by
163 means of fermentation possibly increases during mechanical/physical pretreatment. Further, it
164 can be observable that pretreatment by mechanical processes may raise the temperature of
165 biomass materials to about 70 °C. Physical methods for lignocellulosic complex structure
166 mainly include mechanical shredding (grinding *via* chipping, milling); steam explosion &
167 AFEX (Ammonia fiber/freeze expansion), pyrolysis, radiation energy-based microwaves,
168 pulsed electric field and ultrasound techniques.

169

170 **3.1.1. Mechanical shredding and Pyrolysis**

171 Mechanical shredding (grinding *via* chipping, milling) for soft biomass at a
172 temperature of about 50–70 °C) leads to rupture the lignocellulosic fibers and thereby reduces
173 the period of time duration to digest the materials upto about 23–59% for further treatment to
174 yield fermentative bio-H₂ (Guo et al., 2012; Singh et al., 2022). The fractionation of the
175 shredded materials by means of sieves system makes the particles finer then it consequently
176 leads to an effective hydrolytic process. Further, it can provide nonchemical, green route
177 towards the lignocellulosic pretreatment with no production of unwanted products that assists
178 simultaneously the downstream conversion and processing of the lignocellulosic components
179 (Martin-Sampedro et al., 2012). Though such an overall mechanical pretreatment process is
180 energy-intensive and, thereby one should bring its application for a reasonable raise in the
181 output of final energy only. Pyrolysis is an alternative pretreatment technique for biomass
182 materials but not to produce bio-H₂, instead a mixture of syn-gas and bio-oil (Karimi and
183 Taherzadeh, 2016; Singh et al., 2022). It mainly consists of the thermo-chemical
184 disintegration of biomass materials. Such kind of decomposition begins at about 200 °C.

185

186 **3.1.3. Irradiation processes**

187 Microwave is a new pretreatment option to deconstruct the lignocellulosic 3D
188 complex structure using microwaves to yield bio-H₂ after suitable fermentation of the
189 biomass. Microwaves applied can be suspended in an acidic (1%, 2% / 3% H₂SO₄ (sulfuric

190 acid) or alkaline solution NaOH (sodium hydroxide) that results in an effective increase in the
191 extent of delignification of about 12–30 % (Diaz et al., 2013; Singh et al., 2022). The
192 application of microwave radiation for 5 min on sugarcane bagasse with water (distilled),
193 acid of phosphorus (H_3PO_3 ; pH=3.0) and glycerol of about 10 % indicates that 5.4 % (w/w)
194 fractions of lignin and 11.3 % (w/w) fractions of xylan are disintegrated. In addition, after 24
195 h of incubation the sugarcane bagasse can be treated with microwaves to achieve a high yield
196 by means of the enzymatic hydrolysis of hemicelluloses (22.4 %) and celluloses (40.2 %) (Singh et al., 2022). The pulsed electric field in the form of γ radiation possesses highly
197 penetrating power (Kortei and Wiafe–kwagyan, 2014; Singh et al., 2022). Thereby, it can be
198 applied to thick materials, and it results in the biomass degradation to overcome biomass
199 recalcitrance, followed by solubility increase and decrease in mechanical strength.
200 Conversely, this technique has not been applied in industrial scale, owing to its costs and
201 environmental as well as some safety issues. Among the non–thermal technologies pulsed
202 electric fields (PEF) is an emerging one though that has not been extensively studied. It is
203 owing to the fact that the precise mechanisms by pulsed electric fields are not well
204 understood. However, to achieve many of these processes require very high treatment
205 intensities, and duration from microseconds to milliseconds may cause temporary effects only
206 (Kortei and Wiafe–kwagyan, 2014; Singh et al., 2022). Moreover, inactivating pulsed electric
207 field is the safety measure as per the International guidelines and national safety standards for
208 electromagnetic fields, which are developed on the basis of the current scientific knowledge.
209 I- γ radiation has high potential, though its development and commercialization has been
210 obstructed in the favor of public perceptions. Furthermore, the employment of ultrasonication
211 of frequency 20–40 kHz for biomass pretreatment obviously results in decomposition of the
212 lignocellulosic biomass structures by means of loosening, swelling, and rupturing of fibrils
213 *via* breaking of inter molecular hydrogen linkages (Kucharska et al., 2018) for producing
214 fermentative bio- H_2 , more effectively. Conversely, the economic viability on the
215 fermentation to yield bio- H_2 obviously can be led by mechanical pretreatment, correlated to
216 high energy operations for the mechanical biomass chipping fragmentation (Kucharska et al.,
217 2018).

219

220

221

222

223 3.2. Chemical Pretreatment for Lignocellulosic Biomass

224 Generally, the chemical pretreatment for lignocellulosic biomass (LCB) materials
225 processes are more widely utilized than other physical or biological methods, since, they are
226 more effective as well as enhance the biodegradation of complex LCB materials to yield
227 bio-H₂. The common chemicals such as H₂SO₄, HCl, HNO₃, H₃PO₄, HCOOH, CH₃COOH,
228 NaOH, KOH, Ca(OH)₂, NH_{3(aqu)}, H₂O₂, *etc.*, are widely utilized in this pretreatment process.

230 3.2.1. Acid pretreatment

231 In acid pretreatment method, when the lignocellulosic biomass materials are
232 pretreated with inorganic and organic acids such as HCl, H₂SO₄, HNO₃, H₃PO₄, formic acid,
233 oxalic acid, maleic acid, *etc.*, generate the hydrogen (H⁺) ions, which breakdown the
234 glucosidic chain bonds present between long cellulose and hemicellulose chain into simple
235 sugar units (Ashokkumar et al., 2022; Baruah et al., 2018; Sahoo et al., 2018; Solarte–Toro et
236 al., 2019). Generally, the acid pretreatment involves either the addition of concentrated acids
237 (30–70 % at < 100 °C) or dilute acids (0.2 – 2.5 w/w % or 0.5 – 10 % v/v at 120 – 250 °C) to
238 the LCB materials (Badiei et al., 2014). Dilute H₂SO₄ pretreatment is commonly used for
239 poplar, switch grass, spruce, and corn stover feedstocks. The conc. acid pretreatment can
240 accelerate a high sugar conversion rate (> 90 %) and these acids are more toxic as well as
241 corrosive in nature. Also, the utilization of conc. acids causes the undesired cellulose
242 degradation that is leading to produce huge amount of inhibitory products such as furfurals,
243 aldehydes, 5–hydroxymethyl furfural and phenolic acids. Also, the recovery of acids after
244 hydrolysis process leads to the further treatment process (Amin et al., 2017). Hence, the
245 effective acid pretreatment process involves the selection of acids as mild or dilute acids can
246 be utilized to breakdown the LCB materials into high conversion rate of sugar unit in an
247 economical as well as environmental friendly manner with low generation of inhibitors
248 (Baruah et al., 2018; Ravindran and Jaiswal, 2016; Sahoo et al., 2018; Zheng et al., 2014).
249 Sahoo et al., (Sahoo et al., 2018) reported the effect of dilute H₂SO₄ (0.4 %) and NaOH (1 %)
250 pretreatment on wild rice grass (*Zizania latifolia*) for enzymatic hydrolysis and showed 163
251 and 92 mg sugar g⁻¹ respectively. This study proves the dilute mineral acids pretreatment
252 process is more effective than alkali methods. Furthermore, the organic acids such as oxalic,
253 maleic, citric and formic acids are more efficient than dilute mineral acids for LCB
254 pretreatment for efficient industrial scale fermentative production of bio-H₂ (Baruah et al.,
255 2018).

256 3.2.2. Alkaline pretreatment

257 Alkaline or base pretreatment involves the addition of alkaline reagents or bases (such
258 as NaOH, KOH, Ca(OH)₂, NH₄OH, *etc*) to lignocellulosic biomass materials leading to an
259 increase of internal surface by swelling, decrease of cellulose crystallinity & polymerization,
260 destruction of chemical links between lignin and other polymer units i.e., cleavage of ester
261 and other linkages between lignin and hemicellulose or other carbohydrate moieties, lignin
262 breakdown, solvation of hemicellulose *etc* (Amin et al., 2017; Ashokkumar et al., 2022; Kim
263 et al., 2016; Nahak et al., 2022), as a result a high conversion hydrolysis rate of cellulose into
264 fermentable sugar units either by enzymatic or microorganisms hydrolysis. Generally, the
265 alkaline pretreatment is more effective for hardwood, agricultural residues, herbaceous crops,
266 *etc* with low content of lignin. However, the excessive use of NaOH may cause inhibition of
267 anaerobic digestion (AD) process, especially by methanogenesis and also leads to soil
268 salination as well as water pollution (Kumari and Singh, 2018). Yuan et al. (Yuan et al.,
269 2018), investigated the NaOH and Na₂CO₃ pretreatments on wheat straw at 0 °C for 6 h and
270 showed a solid dissolution efficiency of 86.7 and 91.1 %, respectively. They also showed an
271 improved lignin solubilization as well as hydrolysis of cellulose and hemicellulose that
272 obviously leads to increase the biogas generation. Shen et al., (Shen et al., 2017) reported that
273 NaOH pretreatment on vinegar residue (VR) showed an increased CH₄ yield (205.86 mL g⁻¹
274 at 3% NaOH), that is 54 % higher than the untreated VR. Zhu et al.,(Zhu et al., 2010)
275 reported that over 37 % of biogas can be produced from corn stover by NaOH pretreatment
276 than untreated ones. Shah and Tabassum (Shah and Tabassum, 2018) investigated the lime
277 [Ca(OH)₂] pretreatment on corn cob residue accelerates the digestion process followed by
278 removal of lignin and enhances the biogas productions to 2 times higher than the untreated
279 ones. The major benefit of alkaline pretreatment is efficient for removal of hemicellulose and
280 lignin, to increase the surface area for further hydrolysis process, but this pretreatment causes
281 several issues, especially long process time, difficult reclamation of salt formation, the black
282 liquor and high energy input for hydrolysis (Ashokkumar et al., 2022; Shirkavand et al.,
283 2016; Vu et al., 2020). Effects of acidic and alkaline pretreatments on bio-H₂ production are
284 given in Table 1.

285

286

287

288

289 Table 1. Effects of acid and alkali on bio-H₂ production through inoculum pretreatment [Adopted from modified Ref. (Bundhoo et al.,
 290 2015)].
 291

Inoculum pretreatment	Pretreatment Conditions	Yield of bio-H ₂	References
Anaerobic inoculum	Substrate: Glucose Acid: 2.0 M HCl pH: 3.0 (24 h)	Control: 1.54 meq mol ⁻¹ glucose Treated: 3.00 meq mol ⁻¹ glucose Yield : + 94.80 %	(Chaganti et al., 2012)
	Substrate: Glucose Alkali: 3.0 M NaOH pH: 11.0 (24 h)	Control: 1.54 meq mol ⁻¹ glucose Treated: 2.80 meq mol ⁻¹ glucose Yield : + 81.80 %	
Activated sludge	Substrate: Glucose Acid: 1 M HCl pH: 3.0 (24 h)	Control: 0.38 mol mol ⁻¹ glucose Treated: 1.51 mol mol ⁻¹ glucose Yield : + 297.40 %	(S. Chang et al., 2011)
	Substrate: Glucose Alkali: 1 M NaOH pH: 10.0 (24 h)	Control: 0.38 mol mol ⁻¹ glucose Treated: 1.34 mol mol ⁻¹ glucose Yield : + 252.60 %	
Anaerobic inocula	Substrate: Glucose Acid: HClO ₄ pH: 2.0 (10 min)	<i>Without pre-acidification</i> Control: 60.5 ml Treated: 311.0 ml Yield : + 414.0 %	(Cheong and Hansen, 2006)

		<i>With Pre-acidification (10 M HCl)</i>	
		Control: 32.6 ml	
		Treated: 320.2 ml	
		Yield : + 882.20 %	
Sludge	Substrate: Glucose	Control: 0.7 mol mol ⁻¹ glucose	(Elbeshbishy et al., 2010)
	Acid: 1 N HCl	Treated: 1.11 mol mol ⁻¹ glucose	
	pH: 3.0 (24 h, 4 °C)	Yield : + 58.60 %	
	Substrate: Glucose	Control: 0.7 mol mol ⁻¹ glucose	
	Alkali: 1 N NaOH	Treated: 0.68 mol mol ⁻¹ glucose	
	pH: 10.0 (24 h, 4 °C)	Yield : - 2.90%	
	Substrate: Corn stover hydrolysate	Control: 2.7 mmol g ⁻¹ sugar _{used}	(Zhang et al., 2011)
	Acid: 1.0 M HCl	Treated: 3.21 mmol g ⁻¹ sugar _{used}	
	pH: 3.0 (24 h)	Yield : + 18.90 %	
	Substrate: Corn stover hydrolysate	Control: 2.7 mmol mmol g ⁻¹ sugar _{used}	
	Alkali: 1.0 M NaOH	Treated: 4.45 mmol mmol g ⁻¹ sugar _{used}	
	pH: 12.0 (24 h)	Yield : + 64.80 %	
Methanogenic granules	Substrate: Glucose	Control: 0.42 ml g ⁻¹ glucose	(Hu and Chen, 2007)
	Acid: 0.1 N HCl	Treated: 0.00 ml g ⁻¹ glucose	
	pH: 3.0 (24 h)	Yield : - 100.00 %	
Sewage sludge	Substrate: Glucose	Control: 124.99 ml g ⁻¹ glucose	(Hu and Chen, 2007)

	Acid: 0.1 N HCl pH: 3.0 (24 h)	Treated: 89.01 ml g ⁻¹ glucose Yield : – 28.80 %	
Marine intertidal sludge	Substrate: Glucose Acid: 1 M HCl pH: 3.0 (10 min, 12 h acclimation) Substrate: Glucose Acid: 1 M NaOH pH: 12.0 (10 min, 12 h acclimation)	Control: 0.2 mol mol ⁻¹ glucose Treated: 0.86 mol mol ⁻¹ glucose Yield : + 330.00 % Control: 0.2 mol mol ⁻¹ glucose Treated: 0.11 mol mol ⁻¹ glucose Yield : – 45.00 %	(Liu et al., 2009)
Anaerobic sludge	Substrate: Cassava stillage Acid: 2.0 N HCl pH: 3.0 (24 h) Substrate: Cassava stillage Alkali: 2 N NaOH pH: 12.0 (24 h) Substrate: Palm oil mill effluent Acid: 6.0 N HCl pH: 3.0 (24 h)	<i>Batch system</i> Control: 65.3 ml g ⁻¹ volatile solids (VS) Treated: 46.5 ml g ⁻¹ VS Yield : – 28.80 % <i>Batch System</i> Control: 65.3 ml g ⁻¹ volatile solids (VS) Treated: 59.0 ml g ⁻¹ VS Yield : – 9.60 % Control: 0.12 mmol g ⁻¹ chemical oxygen demand (COD) Treated: 0.32 mmol g ⁻¹ COD Yield : + 166.70 %	(Luo et al., 2010) (Mohammadi et al., 2011)

	Substrate: Palm oil mill effluent Alkali: 6.0 N NaOH pH: 12.0 (24 h)	Control: 0.12 mmol g ⁻¹ COD Treated: 0.37 mmol g ⁻¹ COD Yield : + 208.30 %	
	Substrate: Glucose Acid: 1.0 M HCl pH: 3.0 (24 h, 25 °C)	Control: 178.6 ml Treated: 227.2 ml Yield : + 27.20 %	(Yin et al., 2014)
	Substrate: Glucose Alkali: 1.0 M NaOH pH: 10.0 (24 h, 25 °C)	Control: 178.6 ml Treated: 402.6 ml Yield : + 125.40 %	
Anaerobic granulated sludge	Substrate: Palm oil mill effluent Acid: 6.0 N HCl pH: 3.0 (24 h)	Control: 11.31 mL g ⁻¹ COD Treated: 16.38 mL g ⁻¹ COD Yield : + 44.8%	(Mohammadi et al., 2012)
	Substrate: Palm oil mill effluent Alkali: 6.0 N NaOH pH: 12.0 (24 h)	Control: 11.31 mL g ⁻¹ COD Treated: 17.81 mL g ⁻¹ COD Yield : + 57.50 %	
Anaerobic digested sludge	Substrate: Sucrose Acid: 1.0 M HCl pH: 3.0–4.0 (24 h)	<i>First batch</i> Control: 0.14 mol mol ⁻¹ hexose Treated: 0.43 mol mol ⁻¹ hexose Yield : + 207.10 % <i>Second batch</i>	(O-Thong et al., 2009)

	Substrate: Sucrose pH: 12.0 (24 h)	Control: 0.3 mol mol ⁻¹ hexose Treated: 0.65 mol mol ⁻¹ hexose Yield : + 116.70 % <i>First batch</i> Control: 0.14 mol mol ⁻¹ hexose Treated: 0.3 mol mol ⁻¹ hexose Yield : + 114.30 % <i>Second batch</i> Control: 0.3 mol mol ⁻¹ hexose Treated: 0.51 mol mol ⁻¹ hexose Yield : + 70.00 %	
Granular anaerobic culture	Substrate: Glucose Acid: 2.0 N HCl pH: 3.0 (24 h) Substrate: Glucose Alkali: 3.0 M KOH pH: 12.0 (24 h)	Control: 0.14 mol mol ⁻¹ glucose Treated: 1.10 mol mol ⁻¹ glucose Yield : + 685.70 % Control: 0.14 mol mol ⁻¹ glucose Treated: 0.83 mol mol ⁻¹ glucose Yield : + 492.90 %	(Pendyala et al., 2012)
Flocculated anaerobic culture	Substrate: Glucose Acid: 2.0 N HCl pH: 3.0 (24 h)	Control: 1.3 mol mol ⁻¹ glucose Treated: 1.59 mol mol ⁻¹ glucose Yield : + 22.30 %	(Pendyala et al., 2012)

	Substrate: Glucose Alkali: 3.0 M KOH pH: 12.0 (24 h)	Control: 1.3 mol mol ⁻¹ glucose Treated: 1.41 mol mol ⁻¹ glucose Yield : + 8.50 %	
Sludge from slaughterhouse	Substrate: Sucrose Acid: 1.0 N HCl pH: 3.0 (24 h) Substrate: Sucrose Acid: 1.0 N HCl pH: 3.0 (24 h)	Control: 1.0 mol mol ⁻¹ sucrose Treated: 2.0 mol mol ⁻¹ sucrose Yield : + 100.00 % Control: 0.7 mol mol ⁻¹ sucrose Treated: 1.0 mol mol ⁻¹ sucrose Yield : + 42.90 %	(Penteado et al., 2013)
Mixed microbial culture	Substrate: Glucose Acid: 1.0 N HCl pH: 3.0 (24 h) Substrate: Glucose Alkali: 1.0 N NaOH pH: 11.0 (24 h)	Control: 180.4 ml Treated: 51.9 ml Yield : - 71.20 % Control: 180.4 ml Treated: 134.1 ml Yield : - 25.70 %	(Ren et al., 2008)
Anaerobic sludge consortium	Substrate: Residual glycerol from biodiesel synthesis Acid: 1.0 M HCl pH: 3.0 (24 h) Substrate: Residual glycerol from biodiesel	Control: 1.20 % mol g ⁻¹ glycerol Treated: 0.49 % mol g ⁻¹ glycerol Yield : - 59.20 % Control: 1.20 % mol g ⁻¹ glycerol	(Rossi et al., 2011)

	synthesis Alkali: 1.0 M NaOH pH: 10.0 (24 h)	Treated: 0.03 % mol g ⁻¹ glycerol Yield : - 97.50 %	
Anaerobic mixed microflora	Substrate: Dairy wastewater Acid: H ₃ PO ₄ pH: 3.0 (24 h)	Control: 0.0018 mmol g ⁻¹ COD Treated: 0.0079 mmol g ⁻¹ COD Yield : + 338.90 %	(Venkata Mohan et al., 2008)
Digested sludge	Substrate: Glucose Acid: 1.0 M HCl pH: 3.0 (24 h) Substrate: Glucose Alkali: 1.0 M NaOH pH: 10.0 (24 h)	Control: 65.7 ml Treated: 96.8 ml Yield : + 47.30 % Control: 65.7 ml Treated: 125.9 ml Yield : + 91.60 %	(Wang and Wan, 2008)

292

293

294

295

296

297

298

299

300

301 3.2.3. *Organosolv pretreatment*

302 The most effective and promising organosolv or organic solvent pretreatment method
303 is performed by the aqueous organic solvents such as alcohols (methanol, ethanol, butanol),
304 acetone, phenol, ethylene glycol, tetrahydrofurfuryl alcohol, *etc* with / without addition of a
305 small amount of inorganic acid catalyst (H_2SO_4 , HCl, oxalic acid) for stimulating the
306 pretreatment efficiency of lignocellulosic biomass materials at specified temperature and
307 pressure (Ashokkumar et al., 2022; Capolupo and Faraco, 2016; Khan et al., 2022; Naik et
308 al., 2021; Ravindran and Jaiswal, 2016). This pretreatment completely removes or solubilizes
309 the hemicellulose and lignin moieties in the LCB but the cellulose fraction remains
310 unaffected during this process *i.e.*, to cleave the linkage of lignin and hemicellulose fractions,
311 which can increase the pore volume and accessible surface area of cellulose. As a result, the
312 lignin moieties are dissolved in the organic solvent phase, while cellulose is recovered as
313 solid (Amiri et al., 2014). In general, lower EtOH / H_2O ratios favor the hemicellulose
314 hydrolysis and enzymatic degradability of pretreated LCB since EtOH inhibits the
315 performance of hydrolytic enzymes. The ethanosolv pretreatment with H_2SO_4 on
316 saccharification of poplar biomass has released upto 78 % of the polysaccharides (Chu et al.,
317 2021). Koo et al., (Koo et al., 2011) investigated the aqueous EtOH (50 % v/v) with 1 %
318 NaOH on *Liriodendron tulipifera* (Tulip tree) at 150 °C for 50 min and showed an increased
319 bioethanol production (after hydrolysis and fermentation steps) significantly to 96 %. Sarkar
320 et al., utilized birch sawdust to pretreat at 200 °C within time duration 15 min. In an air-
321 heated reactor, they mixed the sawdust in 60% ethanol and 1% H_2SO_4 (w/w biomass). The
322 pretreated contents then were separated by means of vacuum filtration from the slurry.
323 Consequently, washed with 1.1 L 60% of v/v ethanol/water mixture and finally dried in an
324 oven at 50 °C, overnight. The collected filtrate was used to produce acidogenic fermentative
325 green bio- H_2 (121.4 mL/gVS) (Sarkar et al., 2022). By comparing with other pretreatments,
326 organosolv pretreatment process has many advantages such as ease of recovery of solvents by
327 distillation, low environmental impact, and recovery of high quality lignin as high value
328 added by-product.

329

330 3.2.4. *Ozonolysis pretreatment*

331 In this pretreatment method, the powerful oxidant say ozone (O_3) is sparged into LCB
332 materials, the lignin and hemicellulose contents are degraded but the cellulose fraction is not
333 at all affected (Bensah and Mensah, 2013; Kucharska et al., 2018). The lignin is now

334 oxidized into soluble low molecular weight carboxylic acid compounds such as AcOH,
335 HCOOH, *etc.* The efficiency of enzymatic hydrolysis treatment of LCB by O₃ has enhanced
336 upto 5–folds and also forms no toxic hydrolysis end–products. Silverstein et al., (Silverstein
337 et al., 2007) studied the ozone pretreatment of cotton stalk (10 5 w/v; Temp. 4 °C; Time 30–
338 90 min) showed the reduced lignin content of 11.97–16.60 % and the solubilization of xylan
339 (1.9–16.7 %) and glucan (7.2–16.6 %), which is comparatively lower by this treatment than
340 alkali NaOH process. The great merit for this pretreatment method is no generation of
341 inhibitors i.e., any toxic residues are not generated, however, this method is more expansive
342 than the others. García–Cubero et al., (García–Cubero et al., 2009) reported the improved
343 enzymatic hydrolysis yields of wheat and rye straw upto 89% and 57% respectively, while
344 for the untreated wheat and rye straw the enzymatic hydrolysis yields were 29 % and 16 %
345 respectively.

346

347 **3.2.5. Oxidation pretreatment**

348 In this method, the powerful oxidizing agents like hydrogen peroxide (H₂O₂) or
349 alcoholic solution of peracetic acid are widely being employed for the pretreatment of LCB
350 materials i.e., the oxidant completely dissolves the lignin and amorphous cellulose, while
351 hemicellulose fractions undergo dissolution but the crystalline cellulose content is not
352 dissolved in it (Kucharska et al., 2018). The LCB materials with H₂O₂ generate •OH radicals,
353 which vigorously oxidize as well as degrade lignin fraction. The optimal dosage of H₂O₂ is
354 2.15 % (v/v) at 35 °C and showed effective hydrolysis of LCB materials (Kucharska et al.,
355 2018). The wet oxidation pretreatment of lignocellulosic biomass is done at 195 °C for 10–20
356 min (Anu et al., 2020) with the help of an oxidizer. This pretreatment method is a rapid and
357 effective processes but the formation of inhibitors during fermentation process is its main
358 demerit. The whole hemicellulose and ~ 50 % of lignin fractions present in the LCB materials
359 have been solubilized by treatment with 1–2 % H₂O₂ at temperature of 25–30 °C. Pedersen
360 and Meyer (Pedersen and Meyer, 2009) studied the pretreated of wheat straw with wet
361 oxidation method and showed the yield of 400 and 200 g/kg dry matters for glucose and
362 xylose fractions, respectively followed by enzymatic hydrolysis at 50 °C after 24 h.

363

364 **3.2.6. Ionic liquids (ILs) pretreatment**

365 Ionic liquids (ILs) are thermally stable organic salts composed of cations (such as
366 imidazolium, aliphatic ammonium, pyridinium, alkylated phosphonium, sulfonium ions, *etc*)

367 and anions (such as acetate, chloride, bromide, sulphate, methanoate, nitrate, sulphate,
368 triflate, *etc*) in the liquid state with lower melting point (< 100 °C) and low vapour pressure,
369 as well (Baruah et al., 2018; Behera et al., 2014; Bensah and Mensah, 2013; Brandt et al.,
370 2013; Yoo et al., 2017). ILs is also act as green solvents (GSs) because they possess low
371 vapour pressure, melting point, non-volatility, non-toxicity, high thermal and chemical
372 stability, *etc* (Yoo et al., 2017). During the ILs pretreatment process, both anions and cations
373 form a strong inter- and intramolecular hydrogen bonding with cellulose and other
374 carbohydrate hydroxyl groups in the LCB materials. As a result, the cellulose moiety
375 dissolution increases in presence of electron-withdrawing groups in the alkyl chains of IL
376 cations, hence, the cellulose moiety can undergo precipitation and the lignin can be dissolved
377 in ILs (Chen et al., 2017; Yoo et al., 2017). Some of the ILs like 1-ethyl-3-
378 methylimidazolium diethyl phosphate-acetate, 1-butyl-3-methylimidazoliumacetate, 1-
379 butyl-3-methylimidazoliumchloride, 1-butyl-3-methylimidazoliumacetate, 1-benzyl- 3-
380 methylimidazoliumchloride, 1-butyl-3-methylimidazoliummethylsulfate, 1-ethyl-3-
381 methylimidazoliumgroups, 1,3- dimethylimidazolium groups, cholinium amino acids,
382 cholinium acetate, 1-allyl-3-methylimidazolium chloride, *etc.*, are widely utilized for the
383 treatment of rice husk, water hyacinth, rice straw, kenaf powder, poplar wood, wheat straw,
384 and pine (Behera et al., 2014; Brandt et al., 2013; Kucharska et al., 2018; Shirkavand et al.,
385 2016). The most popular IL is imidazolium-based salts namely Amimcl (1-allyl-3-
386 methylimidazolium chloride) and Bmimcl (1-butyl-3-methylimidazolium chloride), which
387 may be effectively applied for cellulose dissolution when the temperature is < 100 °C (Baruah
388 et al., 2018; Kucharska et al., 2018). Zhi-Guo and Hong-Zhang (Zhang Zhi-guo, 2012)
389 studied the pretreatment of wheat straw with Amim-Cl and showed 100 % increase in
390 glucose yield, when the temperature was increased from 125 to 150 °C at 2 h. Das et al., (Das
391 et al., 2021) reported the enzymatic hydrolysis and ethanol fermentation of several wood
392 materials with two different ionic liquids namely cholinium lysinate [Ch][Lys] and
393 ethanolamine acetate [EOA] [OAc] generated 24–84 % of glucose and 14–80 % of xylose.
394 Rahim et al., (Rahim et al., 2020) investigated the combination of ultrasound irradiation and
395 three different ILs [Emim][OAc], [Emim] [Cl], [Emim][HSO₄] pretreatment of bamboo
396 provided 63.99 % of cellulose and 14.99 % of lignin.

397

398

399

400 3.2.7. *Metal salts pretreatment*

401 The metal salts pretreatment of LCB materials requires a high pressure reactor i.e., the
402 biomass materials are loaded in the reactor along with the metal chlorides such as ZnCl₂,
403 FeCl₃, FeCl₂, CrCl₂, MnCl₂, AlCl₃, *etc* and then heated to 170–180 °C for 20–30 min
404 (Ravindran and Jaiswal, 2016). In addition, the pretreated excess metal salts and other solids
405 are removed by superfine filtration process. Chen *et al.*, (Chen et al., 2014) studied the
406 pretreatment of bagasse with metal chlorides in dilute acidic medium followed by enzymatic
407 hydrolysis and showed a decrease in the total mass of the substrate and most of the sugar
408 moieties are degraded in the acid environment and a major share of them can be appeared in
409 the effluent. Wang et al., (Wang et al., 2014) investigated the hydrolysis of bamboo biomass
410 by dil. HCl in the presence of 1-butyl-3-methylimidazolium chloride with Cu²⁺ ion showed a
411 maximum sugar yield of 67.1 % at 100 °C.

412

413 3.2.8. *Co-solvent enhanced lignocellulosic fractionation (CELF)*

414 In this CELF method, a mixture of tetrahydrofuran (THF) and H₂O is utilized as a
415 monophasic solvent system. This pretreatment process involves the delignification followed
416 by conversion of glucose-rich LCB materials into high value-added fuels, including 5-
417 hydroxymethyl furfural (5-HMF), furfural and levulinic acid (LA) (Ashokkumar et al.,
418 2022). Patri et al., 2021 (Patri et al., 2021) studied the THF co-solvent with mineral H₂SO₄
419 (act as catalyst) on enzymatic hydrolysis of switchgrass biomass, yielded approximately 90 %
420 glucose at 160 °C.

421

422 3.3. *Physico-chemical pretreatment*

423 Among physico-chemical pretreatments such as steam explosion (SE), liquid hot
424 water (LHW), subcritical water (SCW) and ammonia-based methods are promising to
425 breakdown the recalcitrant structure of LCB materials. The liquid hot water and steam
426 explosion processes release very high concentrations of degradation compounds *viz.* furfural,
427 5-hydroxymethylfurfural, acetic acid, formic acid and phenolic compounds that can inhibit
428 enzymes as well as fermentative microorganisms (Anu et al., 2020; Ravindran and Jaiswal,
429 2016). The steam explosion (SE) or autohydrolysis is one of the oldest and effective methods
430 for enzymatic hydrolysis of LCB materials; the LCB materials are pretreated to a high steam
431 pressure (0.7–4.8 MPa) and temperature (160–206 °C) for 1–20 min. At very high
432 temperature and pressure, the steam explosion as well as AFEX (ammonia fiber explosion)

433 can easily disintegrate the cellular components by means of lignocellulosic biomass digestion
434 to yield valid fermentable sugars (Banoth et al., 2017). The main demerit of this steam
435 explosion is the partial degradation of hemicelluloses and thereby producing toxic products.
436 Similar way, the AFEX technique has been considered as efficient process with low content
437 of lignin that is the drawback of this pretreatment process (Sun et al., 2002). Baral and Shah
438 (Baral and Shah, 2017) reported the steam explosion pretreatment of corn stover to produce
439 113.5 million liters butanol per year. Barbanera et al., (Barbanera et al., 2015) investigated
440 the glucose yield on olive tree prunes through steam explosion method, the maximum glucose
441 yield, up to 86 % was achieved at experimental conditions (Temp.: 201 °C, Pressure: 0.86
442 MPa; Time: 15 min). Vivekanand et al., (Vivekanand et al., 2014) reported the combined
443 sequential SO₂ with steam explosion methods, followed by enzymatic hydrolysis that showed
444 more effective polysaccharide conversion upto of 81 %. The LHW pretreatment is an ideal
445 method for the lignocellulose substrates where the addition of chemicals for delignification
446 can result in effective utilization of the biomass. The process is performed only in the
447 customized high pressure reactor. This method is similar to the steam explosion method and
448 this method does not require corrosion resistant reactors or any chemicals and there is no
449 formation of toxic components (Jiang et al., 2015; Ravindran and Jaiswal, 2016). Muharja et
450 al. (Muharja et al., 2018) studied the combined green process of subcritical water (SCW) and
451 enzymatic hydrolysis for bio-H₂ fermentation from coconut husk and the maximum bio-H₂
452 yield, up to 0.279 mol/mol by consumption of sugar, which is lower than the other works.
453 Further, ammonia (NH₃) is an effective agent for the pretreatment of LCB materials. There
454 are three different ammonia-based methods namely (i) ammonia fiber explosion (AFEX), (ii)
455 ammonia recycled percolation (ARP) and (iii) soaking aqueous ammonia (SAA). The AFEX
456 method is a novel advancement technology for the production of fermentable simple sugar
457 units from LCB materials over conventional alkaline processes (Naik et al., 2021; Raj et al.,
458 2022; Ravindran and Jaiswal, 2016). Also, the AFEX pretreatment is most appropriate
459 method for preventing cellulase adsorption to lignin. The AFEX process can be efficiently
460 employed for low-lignin LCB materials like switchgrass, corn stover, Miscanthus, *etc.*,
461 showed > 90 % of glucose yield, during simultaneous saccharification and fermentation
462 process. After the completion of pretreatment, the vaporized NH₃ has been collected,
463 recycled and reused again. Jin et al (Jin et al., 2016) reported that the Great Lakes Bioenergy
464 Laboratories in the US have demonstrated the AFEX pretreatment method for cellulosic
465 ethanol production, which reduced enzyme loading by 66 % and also increased EtOH

466 productivity by 129 %. In an ARP pretreatment process, the poplar wood is soaked in 15 %
467 of NH_3 (aqu.) for 1 h at 40 °C and the pressure was increased to 20 bar. After increasing the
468 temperature upto 180 °C, more liquid extracting was percolated at the rate of 3 ml/min for 90
469 min. In this ARP method, the removal of lignin has been achieved 87 % (Naik et al., 2021).
470 The SAA method also reduces or partially eliminates the lignin fraction from LCB materials.
471

472 3.4. *Biological pretreatment*

473 Biological pretreatment process is more superior to the other methods (Anu et al.,
474 2020) because this method offers numerous advantages such as low energy, low capital cost,
475 decreases in the dependence on chemicals, etc., but main disadvantage is the low hydrolysis
476 rate. During the biological pretreatment of LCB materials, the microorganisms such as
477 bacteria, fungi, enzymes, metabolites from enzymes, etc are playing a vital role before the
478 enzymatic hydrolysis of LCB components (Dey et al., 2022; Hassan et al., 2018). The key
479 biological processes are delignification and saccharification. Generally, the microorganisms,
480 such as brown, white, and soft rot fungi have widely been utilized to degrade the LCB
481 materials to produce fermentative bio- H_2 (Dey et al., 2022; Hassan et al., 2018). Certain
482 microorganisms are present in nature, which exhibit cellulolytic and hemicellulolytic
483 abilities. White rot is able to degrade lignin moieties, present in the LCB materials, which is
484 due to the presence of lignin degrading enzymes like peroxidases and laccases. Brown rot
485 commonly attacks the cellulose content, whereas white as well as soft rot target both lignin
486 and cellulose contents of LCB. Furthermore, the soft rot fungi are efficiently degrading the
487 wood polysaccharides however; the alteration of lignin is limited extent only. The commonly
488 utilized white rot fungi like *Cyathus stercoreus*, *Phanerochaete chrysosporium*, *Pleurotus*
489 *ostreatus*, *Ceriporiopsis subvermispota*, *Ceriporia lacerata*, *Pycnoporus cinnabarinus*,
490 *Cyathus stercolerus*, *Cyathus cinnabarinus*, *Ceriporia lacerata*, *Ceriporiopsis*
491 *subvermispota*, *Pycnoporus cinnabarinus*, *Pleurotus ostreatus*, *Trametes pubescens*, etc., are
492 frequently applied to degrade lignin because these species contain lignin degradation
493 enzymes, including peroxidase and laccase (Anu et al., 2020; Hassan et al., 2018). In addition
494 to some *Basidiomycetes* species, such as *Bjerkandera adusta*, *Irpex lacteus*, *Fomes*
495 *fomentarius*, and *Trametes versicolor* are widely utilized for breaking down of the
496 lignocellulosic materials (Peng et al., 2012). The degradation of lignin by lignolytic enzymes,
497 such as lignin peroxidase, manganese peroxidase and versatile peroxidase, are generated from
498 various microorganisms, which also degrading the lignin structure completely by increasing

499 the phenolic compounds (Baruah et al., 2018; Raj et al., 2022). Suhara et al.,(Suhara et al.,
500 2012) studied the pretreatment of the bundles of bamboo with *Punctularia* sp. and showed an
501 enhanced in the total sugar upto 60.3 % at the same time the lignin content was also reduced.
502 Chang *et al.*, (K. L. Chang et al., 2011) investigated the enzymatic hydrolysis of rice straw
503 with xylanase and cellulase showed a high hydrolysis yield of 84 % with productivity of
504 371.91 g glucose/kg of dry rice straw. Recently, the isolated thermophilic
505 *Thermoanaerobacterium* sp. strain F6 produced 1822.6 and 826.3 mL H₂/L of hydrogen
506 using corn cob and sugarcane bagasse respectively (Jiang et al., 2019).

507

508 3.5. *Nanotechnical pretreatment*

509 Nanotechnology-based pretreatment on lignocellulosic biomass structures is an
510 important methodology to yield bio-H₂. Since the reagents can be easily recycled and
511 reutilized, so it reduces the cost of the process (Chandel et al., 2022). The type of acid-
512 functionalized magnetic nanoparticles (AMNPs) is applicable to the pretreatment of LCB.
513 The AMNPs utilization to enzymatic immobilization, functionalization by means of
514 microbes/chemicals is an alternative to the traditional pretreatment techniques for
515 lignocellulosic biomass. Reusable nature of AMNPs and enzymes obviously is the cost-
516 effective and eco-friendly systems. Nano-sized shear hybrid alkaline (NSHA) catalysts also
517 often utilized for pretreatment techniques for lignocellulosic biomass. The nano-sized metal
518 particles enter into the lignocellulosic cell wall, thereby interaction with biomass component
519 molecules to generate carbohydrates (Abdul Razack et al., 2016; Amin et al., 2017).

520

521 3.5.1. *AMNPs pretreatment*

522 AMNPs possess higher affinity for hydrolyzed lignocellulosic biomass materials,
523 these are also named as solid acid nanocatalysts. Their reusability with strong magnetic
524 nature has added beneficial role in chemical techniques (Peña et al., 2014). By the year of
525 2011, sulfonated MNPs were synthesized to hydrolyse the lignocellulosic biomass structure.
526 Similarly, such functionalized MNPs significantly possess better stability and enhance the
527 catalysis process for bio-fuel production (Wang et al., 2020) .

528

529 3.5.2. *NSHA pretreatment*

530 NSHA catalysts mainly involve in a nano range application, thereby a high shearing
531 of lignocellulosic biomass materials can be performed to remove the lignin molecules for

532 degradation. It has been suggested that NSHA system plays an important role in both
533 saccharification and refineries. Functionalization of NSHA system can be enhanced with
534 certain additives namely PDAC [Poly(diallyldimethylammonium chloride)] and are utilized
535 in the degradation of lignocellulosic biomass constituents. Such kind of produced charged
536 components function as polyelectrolytes to modify surface of the cellulose and thereby
537 stabilization of the lignin occurs. It has been shown that there is generation of globular
538 complexes with lignin components by means of PDAC, and it can alter the biomass cell wall
539 morphology. Further, the PDAC polyelectrolyte reduces utilization of chemical reagents
540 necessitated by the pretreatment of lignocellulosic biomass constituents (Dey et al., 2022).

541

542 **3.6. Role of nano-materials in bio-H₂ production**

543 Production of bio-H, using nano-materials in the bio-fuel industry is very attractive
544 owing to its effective recovery of products (Dey et al., 2022). In such case, the reactions can
545 be performed by metal nano particles (NPs) like Ni(nickel)/Fe(iron) materials. These nano-
546 materials can act as cofactors (like hydrogenase), consequently reduces the exchange of
547 H⁽⁺⁾(protons) (Dey et al., 2022). The function of the microbes has been greatly influenced by
548 increasing the metal NPs concentration to yield bio-H. Such a nano-approach improves the
549 rate of e⁽⁻⁾(electron) transfer that suitably improves the metabolic activity of the micro-biota.
550 It has also been demonstrated that the metal NPs can improve the production of bio-H₂ in
551 acidic pH, moreover the substrate concentration increases with decrease of bio-H₂
552 production, *i.e.*, inverse effect. It was found that the metal oxide NPs can increase 4.5 times
553 of the bio-H₂ production, as compared to normal synthetic processes. Similar way with iron
554 NPs (0.2 g/L), nearly a 33% increase in the bio-H₂ production was observed in sugar
555 (sucrose) medium (Han et al., 2016). Further, 260% conversion of sugar composition by
556 means with a combination of lignocellulosic substrates and Ti(titanium) NPs. Though, the
557 impact on dark fermentation of bio-H₂ production by means of nano-material is still not
558 known clearly (Dey et al., 2022). Further, the main disadvantage of valuable nano-materials
559 assisted technique is its slow rate of yield. It was found that nearly about 35% of
560 lignocellulosic components only converted effectively to bio-H₂ and the residues produce
561 some other by-products. Thereby, there a necessity is to upgrade the technique for industrial
562 production of bio-H₂ by lignocellulosic substrates *via* improvement/introduction of suitable
563 strain as well as nano-materials.

564

565 **Table 2. Production of bio-H₂ by NPs from lignocellulosic materials (Adopted**
 566 **and modified from Ref. (Dey et al., 2022).**

567

Nanomaterials	Microbes / Natural substrate or enzyme used	Bio-Hydrogen production	References
Iron	<i>Enterobacter</i> sp. and <i>Clostridium</i> sp. / Grass	80.70 ml / h, 73.10 %	(Yang and Wang, 2018)
	Mesophilic culture / Starch	200.00 %	(Taherdanak et al., 2016)
	Anaerobic sludge / Sugarcane bagasse	69.00 %	(Reddy et al., 2017)
	<i>Enterobacter aerogenes</i> / Cassava starch	92.00 %	(Lin et al., 2016)
	Anaerobic sludge bacteria / Molasses waste	43.00 %	(Gadhe et al., 2015)
	Thermophillic anaerobic mixed culture / Glucose	53.60 %	(Engliman et al., 2017)
	Anaerobic mixed bacteria / Glucose	33.70 %	(C. Jia et al., 2017; J. Jia et al., 2017)
	<i>Enterobacter cloacae</i> / Glucose	130.00 %	(Nath et al., 2015)
	<i>Clostridium butyricum</i> / Sucrose	32.64 %	(Han et al., 2011)
	<i>Rhodobacter sphaeroides</i> / malate	19.40 %	(Bao et al., 2013)
Nickel	<i>Bacillus anthracis</i> / Palm oil mill eluent	151.00 %	(Mishra et al., 2018)
	Anaerobic sludge bacteria / Molasses waste pH =5.6, T=30–35 °C with 0.0567 wt % of Ni NPs / glucose	24.00 % 22.00 % 2.54 mol	(Gadhe et al., 2015; Mullai et al., 2013)
	Anaerobic mixed bacteria / Glucose (Composite type of carbon)	33.70 %	(C. Jia et al., 2017; J. Jia et al., 2017)
Carbon	Anaerobic sludge/ Glucose (nanotube form of carbon)	50.00 %	(Singh et al., 2018)
	Anaerobic sludge / Sucrose (activated carbon)	62.50 %	(Wimonsong and Nitorisavut, 2015)
	Anaerobic sludge / Sucrose (nano	70.00 %	(Bhatia et al., 2021;

	activated carbon)		Wimonsong and Nitorisravut, 2014)
Noble metals	Silver NPs with <i>Clostridium butyricum</i> / Glucose	67.50 %	(Zhao et al., 2013)
	Gold NPs with Anaerobic sludge / Acetate	–	(Khan et al., 2013)
	Silver with <i>Clostridium butyricum</i> / Glucose	38.00 %	(Beckers et al., 2013; Singhvi and Kim, 2020)
Palladium	Mixed culture / Glucose	9.00 %	(Mohanraj et al., 2014)
Titanium	Anaerobic sludge / Sugarcane bagasse	127.00 %	(Jafari and Zilouei, 2016)

568

569 The outcomes of Table 2 in the view of production of bio-H₂ by means of NPs and
570 different lignocellulosic components mainly are depending on the kind of inter-activity
571 between the biomass material components and nano-catalyst. Further, the rate of electron
572 transfer improves the commercial bio-H₂ yield by making high availability of active surface
573 area with NPs for acceleration of reaction kinetics. Thereby, unwanted oxygen molecules can
574 be removed from the reaction mixture, simultaneously (Dey et al., 2022). Fe(iron)-NPs can
575 play as primary cofactor that can eventually be utilized for the production of bio-H₂ (73%) as
576 the main component for hydrogenase possibly was formed by such a nano system, since it has
577 been associated with the enzymes ferredoxin as well as hydrogenase of the electron transport
578 chain. Some other significant nano system has been formed by Ag(silver), Au(gold),
579 Cu(copper), Pd(palladium), *etc.*, to enhance production of bio-H₂ by means of dark
580 fermentation technique.

581

582 4. Research needs Perspectives and Future Directions

583 The physical pretreatment methods lead to reduce the size of lignocellulosic biomass
584 components, cellulose crystalline index, and raise the availability of the catalytically active
585 sites. This method includes the application of either mechanical shredding *via* grinding
586 (milling and chipping), steam explosion, ammonia based pretreatments (AFEX) or radiation-
587 based techniques *via* ultrasonication, γ , electron beam and microwave radiations (Mankar et
588 al., 2021). In chemical pretreatment, the degradation/decomposition of lignocellulosic
589 biomass components in aquatic phase by means of chemical reactions *viz.* acidic hydrolysis,

590 alkaline hydrolysis, organo–solvent and inorganic salt *via* alkaline salt, metal salt, ionic liquid
591 (IL) and deep eutectic solvent (DES) methods. The eco–friendly and energy efficient green
592 bio–pretreatment processes include the microorganisms *viz.* bacterial, fungal and enzymes to
593 selectively decompose/degrade hemicellulose and lignin moieties, consequently results in an
594 enhanced enzymatic saccharification (Kumar et al., 2020). Though, the application of various
595 kinds of chemical and physical pretreatments possesses their own issues in the bio–
596 conversion of lignocellulosic biomass components. So, introduction of the physico–chemical
597 pretreatment (combination of physical and chemical methods) processes is necessary for
598 industrial applications. Further, these pretreatment processes enhance the solubility of
599 hemicellulose and lignin content for destructuralization of lignocellulose moieties to improve
600 the accessible specific surface on lignocellulosic biomass for enzymes, while with certain
601 slight environmental impacts. The major physico–chemical pretreatment techniques consists
602 of EA: Extractive ammonia and SAA: Soaking aqueous ammonia, supercritical fluid:SCF
603 like $ScCO_2$: Supercritical carbon dioxide: ScH_2O : Supercritical water and $ScNH_3$:
604 Supercritical ammonia explosion, liquid hot water :LHW, hydrothermolysis, uncatalyzed
605 solvolysis, aquasolv and aqueous fraction processes, microwave assisted chemical and
606 SPORL a sulfite pretreatment: (Sulfite pretreatment to overcome recalcitrance of
607 lignocellulose), hydrothermal (HT) explosion and wet air oxidation to overcome recalcitrance
608 of lignocellulose processes (Akhtar et al., 2015; Kumari and Singh, 2018).

609 The exiting challenges in the case of bio–conversion of lignocellulose materials into
610 fermentable sugar moieties and their consequent conversion into high value added bioenergy
611 as well as by–products through various pretreatment approaches. Some of the pretreatment
612 approaches have been utilized in large scale industrial stage, but till now some significant
613 challenges fall in the category of intensively energy requirement, low process efficiency,
614 generation of toxic or environmentally hazardous wastes/inhibitors, perturbation in the
615 overall yield on fermentable sugar moieties, degradation of partial cellulose and
616 lignocellulosic structure, *etc.* (Chauhan, 2020). Now, there is an emerging need for an
617 environmental friendly technology that utilizes the solution of all above challenges *i.e.*, the
618 need of green solvents, low consumption of energy and chemicals, minimization of the water
619 usage, operation with reduced or small particle size, *etc.* The following factors are to be
620 surely considered in order to make LCB (lignocellulose biomass) pretreatment processes
621 efficient as well as effective, they are (i) utilization of large sized LCB particles to minimize
622 the energy application, (ii) operation at very high concentrations of LCB materials to reduce

623 the usage of water as well as energy sources and (iii) operation of integrated process to use
624 the excess heat or steam from other processes of the pretreatment steps. In most of the
625 chemical pretreatment process, the usage of catalysts (both acid, alkali or other chemicals),
626 which are easily miscible in water and the recovery of catalysts from waste water streams are
627 more energy intensive and expensive process *i.e.*, using phosphoric acid pretreatment process
628 results in the formation of very high digestible amorphous cellulose content, but the recovery
629 of acid from aqueous medium is more difficult and expensive process. Further, in some
630 pretreatment processes, the neutralization of chemicals by the additions of acid or base,
631 generate some salts or compounds which cause an additional cost for recovering and
632 recycling with water from consequent processing steps because another major challenges
633 (Janusz et al., 2020, 2017). The LCB pretreatment processes include mechanical processing,
634 microwave irradiation processing, wet oxidation, ozonolysis, hot water and supercritical CO₂
635 and H₂O techniques, no catalysts or expensive chemicals are utilized. So there is no recovery
636 of chemicals or compounds during the processing, but the above techniques need high
637 expensive reactor units (Balan, 2014). Till now, the challenge for the effective enzymatic
638 digestibility of LCB materials is unclear in biological pretreatment process, which is due to
639 the employed complicated structural unit present in the microbes or enzymes. Hence, each
640 pretreatment technology must be upgraded with effective reactor systems with capable of
641 performance at high solid concentrations with large particles and different variety of LCB
642 types and need low energy and water expensive process. So, the utilization of enzyme based
643 LCB pretreatment process overcomes the above challenges more efficiently and effectively
644 than the other technologies (Ponnusamy et al., 2019; Testa and Tummino, 2021).

645 Pretreatment steps for lignocellulosic biomass materials to fermentable sugars are a
646 challenge in the case of large-scale conversion for procuring cost-effective and competitive
647 technically derived products along with very low inhibitory concentration. Agricultural
648 residues have been utilized for industrial bio-fuel production *via* steam explosion, as it is an
649 important technology. This steam explosion in a 50 m³ industrial reactor with corn-stover
650 was performed, to yield 80% of hemicelluloses and then by hydrolysis more than 90 % of
651 celluloses were recovered (Kucharska et al., 2018). Pretreatment with dil. acids is
652 encouraging the production of bio-fuels, as of the biomass possesses high efficiency for the
653 conversion of most of the hemicelluloses into soluble sugars, whereas this process forms
654 furfural like inhibitors compounds. The efficacy of acid hydrolysis enhances the pretreatment
655 *via* optimization of reaction conditions and certain operational parameters *viz.* dosage of acid,

656 pressure, time of retention, solid:liquid ratio and temperature. Silva et al., (Silva and Reis,
657 2016) studied three pretreatment techniques with dil. acids, liquid hot water and AFEX for
658 the production of commercial bio-fuel. Techno-economic analysis has shown that the
659 pretreatment process using LHW turned as a commercial one. The novel approach to lessen
660 the technical issues with the performed pretreatment processes in a single operation, is
661 concerned to combination of those processes *via* mechanical (crushing)-chemical, -electron
662 beam- chemical (alkali), -microwave-chemical, -chemical-steam explosion and physical-
663 biological processes (Chen et al., 2017). The combination of such techniques depends on kind
664 of the biomass feed that integrates the advantage of the concern pretreatment technique. As
665 well, in turn the combination of such processes can considerably progress the effectiveness of
666 enzyme hydrolysis. Binod et al., (Binod et al., 2012) employed a combination of microwave-
667 chemical (-acid and -alkali) pretreatment in place of conventional acid/alkaline pretreatment.
668 The results reveal that the combined treatment enhances the fermentable sugar yield within a
669 short period of time duration. Lai et al., (Lai and Idris, 2016) has suggested low-energy
670 ultrasound-chemical (-alkali) pretreatment for the enhancement of biodegradable nature of
671 lignocellulosic biomass feed. The combination of Ionic liquid-ultrasound process on bagasse,
672 using cholinium IL is biocompatible, showing 80 % of the cellulose and 72% of
673 hemicellulose saccharification along with a little inhibitory effect on enzyme cellulose
674 activity (Ninomiya et al., 2015, 2012). The integration of bioprocesses for the industries to
675 achieve coherent energy efficiency mainly involves the partly bioconversion of spent cooking
676 oil into bio-fuels/cellulose products. Due to the overall cost of production on the
677 lignocellulosic biomass biofuels by fermentation, the wastewater management has given to
678 importance as the biorefinery stillage contains a range of dissolved and unutilized
679 fermentable sugars mainly lignin of about 74.1-79.0 wt. % of the total biomass (Trinh et al.,
680 2013). Consequently, this lignin has been utilized for the production of high-value added
681 products/by direct combustion to supply sufficient energy for the industrial processes. In this
682 regard, fast pyrolysis is currently attracting the interest of researchers since it has the
683 potentiality for the efficient conversion of lignin to high commercially value products like as
684 bio-oil, bio-char, *etc.* (Trinh et al., 2013). But for the production of gaseous bio-fuels
685 towards the industrial application, a specific approach is required to comprehensively analyze
686 the overall operating costs. The production of biogas by anaerobic digestion usually is a
687 heat/energy generating integrated process. Thereby, integrated technologies for the
688 production of bio-H₂ are taken into consideration because utilization of value added products

689 and energy that can be cogenerated, simultaneously as the pretreatment techniques of
690 lignocellulosic biomass is performed before the saccharification, enzymatically. In the case of
691 bio-H₂, high cost and low yields along with comparatively low concentration of fermentation
692 broth are still some major challenges.

693 The chemical pretreatment conventionally is utilizing acids and bases and it can be
694 regarded as a cost-effective process. The by-products formed in this process should be
695 purified and reused in the form of value-added products. Such kind of technique is
696 commercially viable to treat the lignocellulosic biomass feed for bioconversion processes,
697 while bio-fuels and other value added bio-products are derived. The recent familiar
698 pretreatment techniques are generally energy-intensive. Thereby, the development on
699 resourceful and cost-effective pretreatment processes is given significance in an industrial
700 point of view. There, a popular industrial chemical pretreatment technique offers highly
701 digestible biomass feed. Then, the recycling, recovery and utilization of liquids and solids
702 productivity from the wastewater are also accessible, though those processes could be utilized
703 and optimized mainly for bio-ethanol production (Kucharska et al., 2018). The pretreatment
704 technologies for improving production of bio-H₂ from the DF process can be categorized
705 according to their pretreated inoculums/substrates. They can be classified into physical,
706 chemical, physico-chemical, biological and nano-technical pretreatments, based on the
707 biomass used. Amongst, the dissimilar technologies reviewed, acid pretreatments are the
708 mostly studied techniques for the substrates and inoculums. The most suitable emerging
709 techniques over different studies, the hybrid/combined technologies have been given
710 maximum yield. In addition, many pre-techniques have been employed for substrates
711 pretreatment that may eventually form inhibitory compounds thereby can decrease bio-H₂
712 production. As a result, the research needs to find out the best technique for both the
713 substrates and inoculums in industrial scale while a simultaneous consideration towards both
714 energy consumption and technical feasibility in economic aspect. In the case of substrates,
715 most studies have been focused on biomass residues from barley straw, corn stover, wheat
716 straw, *etc.*, food wastes, sludge, and wastewater stream to yield maximum. It has been
717 concluded that among the various pretreatments investigated for such kind of wastes,
718 ultrasound, combined and biological pretreatments have been utilized/employed to procure
719 positive results.

720

721

722 5. Conclusions

723 Effective pretreatment technologies for improving production of bio-H₂ via
724 fermentation from lignocellulosic biomass materials are highly desirable for both energy
725 consumption and technical feasibility towards economic aspect. In addition, utilization of
726 other value-added products *viz.* lignin derived molecules are highly recommended. This type
727 of biorefinery approach is unavoidable for commercialization of lignocellulosic biomass
728 materials.

729

730 Acknowledgement:

731 Young-Kwon Park acknowledges for the support from National Research Foundation
732 of Korea (2021R1A2C3011274).

733

734 References

735

- 736 1. Abbasi, T., Abbasi, S.A., 2010. Biomass energy and the environmental impacts
737 associated with its production and utilization. *Renewable and Sustainable Energy*
738 *Reviews* 14, 919–937. <https://doi.org/10.1016/j.rser.2009.11.006>
- 739 2. Abdul Razack, S., Duraiarasan, S., Mani, V., 2016. Biosynthesis of silver nanoparticle
740 and its application in cell wall disruption to release carbohydrate and lipid from *C.*
741 *vulgaris* for biofuel production. *Biotechnology Reports* 11, 70–76.
742 <https://doi.org/10.1016/j.btre.2016.07.001>
- 743 3. Abraham, A., Mathew, A.K., Park, H., Choi, O., Sindhu, R., Parameswaran, B.,
744 Pandey, A., Park, J.H., Sang, B.I., 2020. Pretreatment strategies for enhanced biogas
745 production from lignocellulosic biomass. *Bioresource Technology* 301, 122725.
746 <https://doi.org/10.1016/j.biortech.2019.122725>
- 747 4. Akhtar, N., Gupta, K., Goyal, D., Goyal, A., 2015. Effect of Hydrothermal
748 Carbonization Reaction Parameters on. *Environmental Progress & Sustainable Energy*
749 35, 489–511. <https://doi.org/10.1002/ep>
- 750 5. Amin, F.R., Khalid, H., Zhang, H., Rahman, S. u, Zhang, R., Liu, G., Chen, C., 2017.
751 Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB*
752 *Express* 7, 72. <https://doi.org/10.1186/s13568-017-0375-4>
- 753 6. Amiri, H., Karimi, K., Zilouei, H., 2014. Organosolv pretreatment of rice straw for
754 efficient acetone, butanol, and ethanol production. *Bioresource Technology* 152, 450–

- 755 456. <https://doi.org/10.1016/j.biortech.2013.11.038>
- 756 7. Anu, Kumar, A., Rapoport, A., Kunze, G., Kumar, S., Singh, D., Singh, B., 2020.
757 Multifarious pretreatment strategies for the lignocellulosic substrates for the
758 generation of renewable and sustainable biofuels: A review. *Renewable Energy* 160,
759 1228–1252. <https://doi.org/10.1016/j.renene.2020.07.031>
- 760 8. Ashokkumar, V., Venkatkarthick, R., Jayashree, S., Chuetor, S., Dharmaraj, S.,
761 Kumar, G., Chen, W.-H., Ngamcharussrivichai, C., 2022. Recent advances in
762 lignocellulosic biomass for biofuels and value-added bioproducts - A critical review.
763 *Bioresource Technology* 344, 126195. <https://doi.org/10.1016/j.biortech.2021.126195>
- 764 9. Azbar, N., Çetinkaya Dokgöz, F.T., Keskin, T., Korkmaz, K.S., Syed, H.M., 2009.
765 Continuous fermentative hydrogen production from cheese whey wastewater under
766 thermophilic anaerobic conditions. *International Journal of Hydrogen Energy* 34,
767 7441–7447. <https://doi.org/10.1016/j.ijhydene.2009.04.032>
- 768 10. Badiei, M., Asim, N., Jahim, J.M., Sopian, K., 2014. Comparison of Chemical
769 Pretreatment Methods for Cellulosic Biomass. *APCBEE Procedia* 9, 170–174.
770 <https://doi.org/10.1016/j.apcbee.2014.01.030>
- 771 11. Balan, V., 2014. Current Challenges in Commercially Producing Biofuels from
772 Lignocellulosic Biomass. *ISRN Biotechnology* 2014, 1–31.
773 <https://doi.org/10.1155/2014/463074>
- 774 12. Balat, M., 2011. Production of bioethanol from lignocellulosic materials via the
775 biochemical pathway: A review. *Energy Conversion and Management* 52, 858–875.
776 <https://doi.org/10.1016/j.enconman.2010.08.013>
- 777 13. Banoth, C., Sunkar, B., Tondamanati, P.R., Bhukya, B., 2017. Improved
778 physicochemical pretreatment and enzymatic hydrolysis of rice straw for bioethanol
779 production by yeast fermentation. *3 Biotech* 7. [https://doi.org/10.1007/s13205-017-](https://doi.org/10.1007/s13205-017-0980-6)
780 [0980-6](https://doi.org/10.1007/s13205-017-0980-6)
- 781 14. Bao, M.D., Su, H.J., Tan, T.W., 2013. Dark fermentative bio-hydrogen production:
782 Effects of substrate pre-treatment and addition of metal ions or L-cysteine. *Fuel* 112,
783 38–44. <https://doi.org/10.1016/j.fuel.2013.04.063>
- 784 15. Baral, N.R., Shah, A., 2017. Comparative techno-economic analysis of steam
785 explosion, dilute sulfuric acid, ammonia fiber explosion and biological pretreatments
786 of corn stover. *Bioresource Technology* 232, 331–343.
787 <https://doi.org/10.1016/j.biortech.2017.02.068>

- 788 16. Barbanera, M., Buratti, C., Cotana, F., Foschini, D., Lascaro, E., 2015. Effect of
789 steam explosion pretreatment on sugar production by enzymatic hydrolysis of olive
790 tree pruning. *Energy Procedia* 81, 146–154.
791 <https://doi.org/10.1016/j.egypro.2015.12.069>
- 792 17. Baruah, J., Nath, B.K., Sharma, R., Kumar, S., Deka, R.C., Baruah, D.C., Kalita, E.,
793 2018. Recent trends in the pretreatment of lignocellulosic biomass for value-added
794 products. *Frontiers in Energy Research* 6, 1–19.
795 <https://doi.org/10.3389/fenrg.2018.00141>
- 796 18. Beckers, L., Hiligsmann, S., Lambert, S.D., Heinrichs, B., Thonart, P., 2013.
797 Improving effect of metal and oxide nanoparticles encapsulated in porous silica on
798 fermentative biohydrogen production by *Clostridium butyricum*. *Bioresource*
799 *Technology* 133, 109–117. <https://doi.org/10.1016/j.biortech.2012.12.168>
- 800 19. Behera, S., Arora, R., Nandhagopal, N., Kumar, S., 2014. Importance of chemical
801 pretreatment for bioconversion of lignocellulosic biomass. *Renewable and*
802 *Sustainable Energy Reviews* 36, 91–106. <https://doi.org/10.1016/j.rser.2014.04.047>
- 803 20. Bensah, E.C., Mensah, M., 2013. Chemical pretreatment methods for the production
804 of cellulosic ethanol: Technologies and innovations. *International Journal of Chemical*
805 *Engineering* 2013. <https://doi.org/10.1155/2013/719607>
- 806 21. Bhatia, S.K., Jagtap, S.S., Bedekar, A.A., Bhatia, R.K., Rajendran, K., Pugazhendhi,
807 A., Rao, C. V., Atabani, A.E., Kumar, G., Yang, Y.H., 2021. Renewable biohydrogen
808 production from lignocellulosic biomass using fermentation and integration of
809 systems with other energy generation technologies. *Science of the Total Environment*
810 765, 144429. <https://doi.org/10.1016/j.scitotenv.2020.144429>
- 811 22. Binod, P., Satyanagalakshmi, K., Sindhu, R., Janu, K.U., Sukumaran, R.K., Pandey,
812 A., 2012. Short duration microwave assisted pretreatment enhances the enzymatic
813 saccharification and fermentable sugar yield from sugarcane bagasse. *Renewable*
814 *Energy* 37, 109–116. <https://doi.org/10.1016/j.renene.2011.06.007>
- 815 23. Brandt, A., Gräsvik, J., Hallett, J.P., Welton, T., 2013. Deconstruction of
816 lignocellulosic biomass with ionic liquids. *Green Chemistry* 15, 550–583.
817 <https://doi.org/10.1039/c2gc36364j>
- 818 24. Bundhoo, M.A.Z., Mohee, R., Hassan, M.A., 2015. Effects of pre-treatment
819 technologies on dark fermentative biohydrogen production: A review. *Journal of*
820 *Environmental Management* 157, 20–48.

- 821 <https://doi.org/10.1016/j.jenvman.2015.04.006>
- 822 25. Capolupo, L., Faraco, V., 2016. Green methods of lignocellulose pretreatment for
823 biorefinery development. *Applied Microbiology and Biotechnology* 100, 9451–9467.
824 <https://doi.org/10.1007/s00253-016-7884-y>
- 825 26. Chaganti, S.R., Kim, D.H., Lalman, J.A., 2012. Dark fermentative hydrogen
826 production by mixed anaerobic cultures: Effect of inoculum treatment methods on
827 hydrogen yield. *Renewable Energy* 48, 117–121.
828 <https://doi.org/10.1016/j.renene.2012.04.015>
- 829 27. Chandel, H., Kumar, P., Chandel, A.K., Verma, M.L., 2022. Biotechnological
830 advances in biomass pretreatment for bio-renewable production through
831 nanotechnological intervention. *Biomass Conversion and Biorefinery* 2024.
832 <https://doi.org/10.1007/s13399-022-02746-0>
- 833 28. Chang, K.L., Thitikorn-amorn, J., Hsieh, J.F., Ou, B.M., Chen, S.H.,
834 Ratanakhanokchai, K., Huang, P.J., Chen, S.T., 2011. Enhanced enzymatic
835 conversion with freeze pretreatment of rice straw. *Biomass and Bioenergy* 35, 90–95.
836 <https://doi.org/10.1016/j.biombioe.2010.08.027>
- 837 29. Chang, S., Li, J.Z., Liu, F., 2011. Evaluation of different pretreatment methods for
838 preparing hydrogen-producing seed inocula from waste activated sludge. *Renewable*
839 *Energy* 36, 1517–1522. <https://doi.org/10.1016/j.renene.2010.11.023>
- 840 30. Chauhan, P.S., 2020. Role of various bacterial enzymes in complete depolymerization
841 of lignin: A review. *Biocatalysis and Agricultural Biotechnology* 23, 101498.
842 <https://doi.org/10.1016/j.bcab.2020.101498>
- 843 31. Chen, H., Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., Han, S., 2017. A
844 review on the pretreatment of lignocellulose for high-value chemicals. *Fuel*
845 *Processing Technology* 160, 196–206. <https://doi.org/10.1016/j.fuproc.2016.12.007>
- 846 32. Chen, L., Chen, R., Fu, S., 2014. Preliminary exploration on pretreatment with metal
847 chlorides and enzymatic hydrolysis of bagasse. *Biomass and Bioenergy* 71, 311–317.
848 <https://doi.org/10.1016/j.biombioe.2014.09.026>
- 849 33. Cheong, D.Y., Hansen, C.L., 2006. Bacterial stress enrichment enhances anaerobic
850 hydrogen production in cattle manure sludge. *Applied Microbiology and*
851 *Biotechnology* 72, 635–643. <https://doi.org/10.1007/s00253-006-0313-x>
- 852 34. Chu, Q., Tong, W., Chen, J., Wu, S., Jin, Y., Hu, J., Song, K., 2021. Organosolv
853 pretreatment assisted by carbocation scavenger to mitigate surface barrier effect of

- 854 lignin for improving biomass saccharification and utilization. *Biotechnology for*
855 *Biofuels* 14, 1–13. <https://doi.org/10.1186/s13068-021-01988-w>
- 856 35. Das, L., Achinivu, E.C., Barcelos, C.A., Sundstrom, E., Amer, B., Baidoo, E.E.K.,
857 Simmons, B.A., Sun, N., Gladden, J.M., 2021. Deconstruction of Woody Biomass via
858 Protic and Aprotic Ionic Liquid Pretreatment for Ethanol Production. *ACS*
859 *Sustainable Chemistry and Engineering* 9, 4422–4432.
860 <https://doi.org/10.1021/acssuschemeng.0c07925>
- 861 36. Dey, N., Kumar, G., Vickram, A.S., Mohan, M., Singhanian, R.R., Patel, A.K., Dong,
862 C.-D., Anbarasu, K., Thanigaivel, S., Ponnusamy, V.K., 2022. Nanotechnology-
863 assisted production of value-added biopotent energy-yielding products from
864 lignocellulosic biomass refinery – A review. *Bioresource Technology* 344, 126171.
865 <https://doi.org/10.1016/j.biortech.2021.126171>
- 866 37. Dharmaraja, J., Shobana, S., Arvindnarayan, S., Vadivel, M., Atabani, A.E.,
867 Pugazhendhi, A., Kumar, G., 2019. Biobutanol from lignocellulosic biomass:
868 Bioprocess strategies. *Lignocellulosic Biomass to Liquid Biofuels* 169–193.
869 <https://doi.org/10.1016/B978-0-12-815936-1.00005-8>
- 870 38. Diaz, A., Le Toullec, J., Blandino, A., De Ory, I., Caro, I., 2013. Pretreatment of rice
871 hulls with alkaline peroxide to enhance enzyme hydrolysis for ethanol production.
872 *Chemical Engineering Transactions* 32, 949–954.
873 <https://doi.org/10.3303/CET1332159>
- 874 39. Elbeshbishy, E., Hafez, H., Nakhla, G., 2010. Enhancement of biohydrogen producing
875 using ultrasonication. *Renewable Energy* 35, 6184–6193.
876 <https://doi.org/10.1016/j.ijhydene.2010.03.119>
- 877 40. Engliman, N.S., Abdul, P.M., Wu, S.Y., Jahim, J.M., 2017. Influence of iron (II)
878 oxide nanoparticle on biohydrogen production in thermophilic mixed fermentation.
879 *International Journal of Hydrogen Energy* 42, 27482–27493.
880 <https://doi.org/10.1016/j.ijhydene.2017.05.224>
- 881 41. Gadhe, A., Sonawane, S.S., Varma, M.N., 2015. Enhancement effect of hematite and
882 nickel nanoparticles on biohydrogen production from dairy wastewater. *International*
883 *Journal of Hydrogen Energy* 40, 4502–4511.
884 <https://doi.org/10.1016/j.ijhydene.2015.02.046>
- 885 42. García-Cubero, M.T., González-Benito, G., Indacochea, I., Coca, M., Bolado, S.,
886 2009. Effect of ozonolysis pretreatment on enzymatic digestibility of wheat and rye

- 887 straw. *Bioresource Technology* 100, 1608–1613.
888 <https://doi.org/10.1016/j.biortech.2008.09.012>
- 889 43. Gómez, X., Fernández, C., Fierro, J., Sánchez, M.E., Escapa, A., Morán, A., 2011.
890 Hydrogen production: Two stage processes for waste degradation. *Bioresource*
891 *Technology* 102, 8621–8627. <https://doi.org/10.1016/j.biortech.2011.03.055>
- 892 44. Goryunov, A.G., Goryunova, N.N., Ogunlana, A.O., Manenti, F., 2016. Production of
893 energy from biomass: Near or distant future prospects? *Chemical Engineering*
894 *Transactions* 52, 1219–1224. <https://doi.org/10.3303/CET1652204>
- 895 45. Guo, F., Fang, Z., Xu, C.C., Smith, R.L., 2012. Solid acid mediated hydrolysis of
896 biomass for producing biofuels. *Progress in Energy and Combustion Science* 38, 672–
897 690. <https://doi.org/10.1016/j.pecs.2012.04.001>
- 898 46. Han, H., Cui, M., Wei, L., Yang, H., Shen, J., 2011. Enhancement effect of hematite
899 nanoparticles on fermentative hydrogen production. *Bioresource Technology* 102,
900 7903–7909. <https://doi.org/10.1016/j.biortech.2011.05.089>
- 901 47. Hassan, S.S., Williams, G.A., Jaiswal, A.K., 2018. Emerging technologies for the
902 pretreatment of lignocellulosic biomass. *Bioresource Technology* 262, 310–318.
903 <https://doi.org/10.1016/j.biortech.2018.04.099>
- 904 48. Hendriks, A.T.W.M., Zeeman, G., 2009. Pretreatments to enhance the digestibility of
905 lignocellulosic biomass. *Bioresource Technology* 100, 10–18.
906 <https://doi.org/10.1016/j.biortech.2008.05.027>
- 907 49. Hu, B., Chen, S., 2007. Pretreatment of methanogenic granules for immobilized
908 hydrogen fermentation. *International Journal of Hydrogen Energy* 32, 3266–3273.
909 <https://doi.org/10.1016/j.ijhydene.2007.03.005>
- 910 50. IEA, 2015. Medium-term renewable energy market report 2015. Market analysis and
911 forecasts to 2020: 270.
- 912 51. Jafari, O., Zilouei, H., 2016. Enhanced biohydrogen and subsequent biomethane
913 production from sugarcane bagasse using nano-titanium dioxide pretreatment,
914 *Bioresource Technology*. <https://doi.org/10.1016/j.biortech.2016.05.007>
- 915 52. Janusz, G., Pawlik, A., Sulej, J., Świdarska-Burek, U., Jarosz-Wilkolazka, A.,
916 Paszczyński, A., 2017. Lignin degradation: Microorganisms, enzymes involved,
917 genomes analysis and evolution. *FEMS Microbiology Reviews* 41, 941–962.
918 <https://doi.org/10.1093/femsre/fux049>
- 919 53. Janusz, G., Pawlik, A., Świdarska-Burek, U., Polak, J., Sulej, J., Jarosz-Wilkolazka,

- 920 A., Paszczyński, A., 2020. Laccase Properties, Physiological Functions, and
921 Evolution. *International Journal of Molecular Sciences* 21, 966.
922 <https://doi.org/10.3390/ijms21030966>
- 923 54. Jia, C., Chen, L., Shao, Z., Agarwal, U.P., Hu, L., Zhu, J.Y., 2017. Using a fully
924 recyclable dicarboxylic acid for producing dispersible and thermally stable cellulose
925 nanomaterials from different cellulosic sources. *Cellulose* 24, 2483–2498.
926 <https://doi.org/10.1007/s10570-017-1277-y>
- 927 55. Jia, J., Zhang, W., Yang, Z., Yang, X., Wang, N., Yu, X., 2017. Novel magnetic
928 cross-linked cellulase aggregates with a potential application in lignocellulosic
929 biomass bioconversion. *Molecules* 22. <https://doi.org/10.3390/molecules22020269>
- 930 56. Jiang, W., Chang, S., Li, H., Oleskowicz-Popiel, P., Xu, J., 2015. Liquid hot water
931 pretreatment on different parts of cotton stalk to facilitate ethanol production.
932 *Bioresource Technology* 176, 175–180. <https://doi.org/10.1016/j.biortech.2014.11.023>
- 933 57. Jiang, Y., Lu, J., Lv, Y., Wu, R., Dong, W., Zhou, J., Jiang, M., Xin, F., 2019.
934 Efficient hydrogen production from lignocellulosic feedstocks by a newly isolated
935 thermophilic *Thermoanaerobacterium* sp. strain F6. *International Journal of Hydrogen*
936 *Energy* 44, 14380–14386. <https://doi.org/10.1016/j.ijhydene.2019.01.226>
- 937 58. Jin, M., Da Costa Sousa, L., Schwartz, C., He, Y., Sarks, C., Gunawan, C., Balan, V.,
938 Dale, B.E., 2016. Toward lower cost cellulosic biofuel production using ammonia
939 based pretreatment technologies. *Green Chemistry* 18, 957–966.
940 <https://doi.org/10.1039/c5gc02433a>
- 941 59. Karimi, K., Taherzadeh, M.J., 2016. A critical review of analytical methods in
942 pretreatment of lignocelluloses: Composition, imaging, and crystallinity. *Bioresource*
943 *Technology* 200, 1008–1018. <https://doi.org/10.1016/j.biortech.2015.11.022>
- 944 60. Khan, M.M., Lee, J., Cho, M.H., 2013. Electrochemically active biofilm mediated
945 bio-hydrogen production catalyzed by positively charged gold nanoparticles.
946 *International Journal of Hydrogen Energy* 38, 5243–5250.
947 <https://doi.org/10.1016/j.ijhydene.2013.02.080>
- 948 61. Khan, M.U., Usman, M., Ashraf, M.A., Dutta, N., Luo, G., Zhang, S., 2022. A review
949 of recent advancements in pretreatment techniques of lignocellulosic materials for
950 biogas production: Opportunities and Limitations. *Chemical Engineering Journal*
951 *Advances* 10, 100263. <https://doi.org/10.1016/j.cej.2022.100263>
- 952 62. Kim, J.S., Lee, Y.Y., Kim, T.H., 2016. A review on alkaline pretreatment technology

- 953 for bioconversion of lignocellulosic biomass. *Bioresource Technology* 199, 42–48.
954 <https://doi.org/10.1016/j.biortech.2015.08.085>
- 955 63. Koo, B.W., Kim, H.Y., Park, N., Lee, S.M., Yeo, H., Choi, I.G., 2011. Organosolv
956 pretreatment of *Liriodendron tulipifera* and simultaneous saccharification and
957 fermentation for bioethanol production. *Biomass and Bioenergy* 35, 1833–1840.
958 <https://doi.org/10.1016/j.biombioe.2011.01.014>
- 959 64. Kortei, N.K., Wiafe-kwagyan, M., 2014. Evaluating the effect of gamma radiation on
960 eight different agro-lignocellulose waste materials for the production of oyster
961 mushrooms (*Pleurotus eous* (Berk .) Sacc . strain P-31) 9, 83–90.
- 962 65. Kucharska, K., Rybarczyk, P., Hołowacz, I., Łukajtis, R., Glinka, M., Kamiński, M.,
963 2018. Pretreatment of lignocellulosic materials as substrates for fermentation
964 processes. *Molecules* 23, 1–32. <https://doi.org/10.3390/molecules23112937>
- 965 66. Kumar, B., Bhardwaj, N., Agrawal, K., Chaturvedi, V., Verma, P., 2020. Current
966 perspective on pretreatment technologies using lignocellulosic biomass: An emerging
967 biorefinery concept. *Fuel Processing Technology* 199.
968 <https://doi.org/10.1016/j.fuproc.2019.106244>
- 969 67. Kumar, G., Dharmaraja, J., Arvindnarayan, S., Shoban, S., Bakonyi, P., Saratale,
970 G.D., Nemestóthy, N., Bélafi-Bakó, K., Yoon, J.J., Kim, S.H., 2019. A
971 comprehensive review on thermochemical, biological, biochemical and hybrid
972 conversion methods of bio-derived lignocellulosic molecules into renewable fuels.
973 *Fuel* 251, 352–367. <https://doi.org/10.1016/j.fuel.2019.04.049>
- 974 68. Kumari, D., Singh, R., 2018. Pretreatment of lignocellulosic wastes for biofuel
975 production: A critical review. *Renewable and Sustainable Energy Reviews* 90, 877–
976 891. <https://doi.org/10.1016/j.rser.2018.03.111>
- 977 69. Lai, L.W., Idris, A., 2016. Comparison of steam-alkali-chemical and microwave-
978 alkali pretreatment for enhancing the enzymatic saccharification of oil palm trunk.
979 *Renewable Energy* 99, 738–746. <https://doi.org/10.1016/j.renene.2016.07.059>
- 980 70. Lin, R., Cheng, J., Ding, L., Song, W., Liu, M., Zhou, J., Cen, K., 2016. Enhanced
981 dark hydrogen fermentation by addition of ferric oxide nanoparticles using
982 *Enterobacter aerogenes*. *Bioresource Technology* 207, 213–219.
983 <https://doi.org/10.1016/j.biortech.2016.02.009>
- 984 71. Liu, H., Wang, G., Zhu, D., Pan, G., 2009. Enrichment of the hydrogen-producing
985 microbial community from marine intertidal sludge by different pretreatment

- 986 methods. *International Journal of Hydrogen Energy* 34, 9696–9701.
987 <https://doi.org/10.1016/j.ijhydene.2009.10.025>
- 988 72. Luo, G., Xie, L., Zou, Z., Wang, W., Zhou, Q., 2010. Evaluation of pretreatment
989 methods on mixed inoculum for both batch and continuous thermophilic biohydrogen
990 production from cassava stillage. *Bioresource Technology* 101, 959–964.
991 <https://doi.org/10.1016/j.biortech.2009.08.090>
- 992 73. Mankar, A.R., Pandey, A., Modak, A., Pant, K.K., 2021. Pretreatment of
993 lignocellulosic biomass: A review on recent advances. *Bioresource Technology* 334,
994 125235. <https://doi.org/10.1016/j.biortech.2021.125235>
- 995 74. Martin-Sampedro, R., Filpponen, I., Hoeger, I.C., Zhu, J.Y., Laine, J., Rojas, O.J.,
996 2012. Rapid and complete enzyme hydrolysis of lignocellulosic nanofibrils. *ACS*
997 *Macro Letters* 1, 1321–1325. <https://doi.org/10.1021/mz300484b>
- 998 75. Mishra, P., Thakur, S., Mahapatra, D.M., Wahid, Z.A., Liu, H., Singh, L., 2018.
999 Impacts of nano-metal oxides on hydrogen production in anaerobic digestion of palm
1000 oil mill effluent – A novel approach. *International Journal of Hydrogen Energy* 43,
1001 2666–2676. <https://doi.org/10.1016/j.ijhydene.2017.12.108>
- 1002 76. Mohammadi, P., Ibrahim, S., Annuar, M.S.M., 2012. Comparative study on the effect
1003 of various pretreatment methods on the enrichment of hydrogen producing bacteria in
1004 anaerobic granulated sludge from brewery wastewater. *Korean Journal of Chemical*
1005 *Engineering* 29, 1347–1351. <https://doi.org/10.1007/s11814-012-0018-z>
- 1006 77. Mohammadi, P., Ibrahim, S., Mohamad Annuar, M.S., Law, S., 2011. Effects of
1007 different pretreatment methods on anaerobic mixed microflora for hydrogen
1008 production and COD reduction from palm oil mill effluent. *Journal of Cleaner*
1009 *Production* 19, 1654–1658. <https://doi.org/10.1016/j.jclepro.2011.05.009>
- 1010 78. Mohanraj, S., Anbalagan, K., Kodhaiyolii, S., Pugalenti, V., 2014. Comparative
1011 evaluation of fermentative hydrogen production using *Enterobacter cloacae* and
1012 mixed culture: Effect of Pd (II) ion and phyto-genic palladium nanoparticles. *Journal*
1013 *of Biotechnology* 192, 87–95. <https://doi.org/10.1016/j.jbiotec.2014.10.012>
- 1014 79. Moreno, J., Dufour, J., 2013. Life cycle assessment of hydrogen production from
1015 biomass gasification. Evaluation of different Spanish feedstocks. *International Journal*
1016 *of Hydrogen Energy* 38, 7616–7622. <https://doi.org/10.1016/j.ijhydene.2012.11.076>
- 1017 80. Muharja, M., Junianti, F., Ranggina, D., Nurtono, T., Widjaja, A., 2018. An integrated
1018 green process: Subcritical water, enzymatic hydrolysis, and fermentation, for

- 1019 biohydrogen production from coconut husk. *Bioresource Technology* 249, 268–275.
1020 <https://doi.org/10.1016/j.biortech.2017.10.024>
- 1021 81. Mullai, P., Yogeswari, M.K., Sridevi, K., 2013. Optimisation and enhancement of
1022 biohydrogen production using nickel nanoparticles - A novel approach. *Bioresource*
1023 *Technology* 141, 212–219. <https://doi.org/10.1016/j.biortech.2013.03.082>
- 1024 82. Nahak, B.K., Preetam, S., Sharma, D., Shukla, S.K., Syväjärvi, M., Toncu, D.C.,
1025 Tiwari, A., 2022. Advancements in net-zero pertinency of lignocellulosic biomass for
1026 climate neutral energy production. *Renewable and Sustainable Energy Reviews* 161.
1027 <https://doi.org/10.1016/j.rser.2022.112393>
- 1028 83. Naik, G.P., Poonia, A.K., Chaudhari, P.K., 2021. Pretreatment of lignocellulosic
1029 agricultural waste for delignification, rapid hydrolysis, and enhanced biogas
1030 production: A review. *Journal of the Indian Chemical Society* 98.
1031 <https://doi.org/10.1016/j.jics.2021.100147>
- 1032 84. Nath, D., Manhar, A.K., Gupta, K., Saikia, D., Das, S.K., Mandal, M., 2015.
1033 Phytosynthesized iron nanoparticles: Effects on fermentative hydrogen production by
1034 *Enterobacter cloacae* DH-89. *Bulletin of Materials Science* 38, 1533–1538.
1035 <https://doi.org/10.1007/s12034-015-0974-0>
- 1036 85. Ninomiya, K., Kamide, K., Takahashi, K., Shimizu, N., 2012. Enhanced enzymatic
1037 saccharification of kenaf powder after ultrasonic pretreatment in ionic liquids at room
1038 temperature. *Bioresource Technology* 103, 259–265.
1039 <https://doi.org/10.1016/j.biortech.2011.10.019>
- 1040 86. Ninomiya, K., Kohori, A., Tatsumi, M., Osawa, K., Endo, T., Kakuchi, R., Ogino, C.,
1041 Shimizu, N., Takahashi, K., 2015. Ionic liquid/ultrasound pretreatment and in situ
1042 enzymatic saccharification of bagasse using biocompatible cholinium ionic liquid.
1043 *Bioresource Technology* 176, 169–174. <https://doi.org/10.1016/j.biortech.2014.11.038>
- 1044 87. O-Thong, S., Prasertsan, P., Birkeland, N.K., 2009. Evaluation of methods for
1045 preparing hydrogen-producing seed inocula under thermophilic condition by process
1046 performance and microbial community analysis. *Bioresource Technology* 100, 909–
1047 918. <https://doi.org/10.1016/j.biortech.2008.07.036>
- 1048 88. Patri, A.S., Mohan, R., Pu, Y., Yoo, C.G., Ragauskas, A.J., Kumar, R., Kisailus, D.,
1049 Cai, C.M., Wyman, C.E., 2021. THF co-solvent pretreatment prevents lignin
1050 redeposition from interfering with enzymes yielding prolonged cellulase activity.
1051 *Biotechnology for Biofuels* 14, 1–13. <https://doi.org/10.1186/s13068-021-01904-2>

- 1052 89. Pedersen, M., Meyer, A.S., 2009. Influence of substrate particle size and wet
1053 oxidation on physical surface structures and enzymatic hydrolysis of wheat straw.
1054 *Biotechnology Progress* 25, 399–408. <https://doi.org/10.1002/btpr.141>
- 1055 90. Peña, L., Xu, F., Hohn, K.L., Li, J., Wang, D., 2014. Propyl-Sulfonic Acid
1056 Functionalized Nanoparticles as Catalyst for Pretreatment of Corn Stover. *Journal of*
1057 *Biomaterials and Nanobiotechnology* 05, 8–16.
1058 <https://doi.org/10.4236/jbnb.2014.51002>
- 1059 91. Pendyala, B., Rao, S., Lalman, J.A., Shanmugam, S.R., Heath, D.D., Lau, P.C.K.,
1060 2012. Pretreating mixed anaerobic communities from different sources : Correlating
1061 the hydrogen yield with hydrogenase activity and microbial diversity. *International*
1062 *Journal of Hydrogen Energy* 37, 12175–12186.
1063 <https://doi.org/10.1016/j.ijhydene.2012.05.105>
- 1064 92. Peng, F., Peng, P., Xu, F., Sun, R.C., 2012. Fractional purification and bioconversion
1065 of hemicelluloses. *Biotechnology Advances* 30, 879–903.
1066 <https://doi.org/10.1016/j.biotechadv.2012.01.018>
- 1067 93. Penteado, E.D., Lazaro, C.Z., Sakamoto, I.K., Zaiat, M., 2013. Influence of seed
1068 sludge and pretreatment method on hydrogen production in packed-bed anaerobic
1069 reactors. *International Journal of Hydrogen Energy* 38, 6137–6145.
1070 <https://doi.org/10.1016/j.ijhydene.2013.01.067>
- 1071 94. Ponnusamy, V.K., Nguyen, D.D., Dharmaraja, J., Shobana, S., Banu, J.R., Saratale,
1072 R.G., Chang, S.W., Kumar, G., 2019. A review on lignin structure, pretreatments,
1073 fermentation reactions and biorefinery potential. *Bioresource Technology*.
1074 <https://doi.org/10.1016/j.biortech.2018.09.070>
- 1075 95. Rahim, A.H.A., Man, Z., Sarwono, A., Muhammad, N., Khan, A.S., Hamzah,
1076 W.S.W., Yunus, N.M., Elsheikh, Y.A., 2020. Probe sonication assisted ionic liquid
1077 treatment for rapid dissolution of lignocellulosic biomass. *Cellulose* 27, 2135–2148.
1078 <https://doi.org/10.1007/s10570-019-02914-y>
- 1079 96. Raj, T., Chandrasekhar, K., Naresh Kumar, A., Kim, S.H., 2022. Lignocellulosic
1080 biomass as renewable feedstock for biodegradable and recyclable plastics production:
1081 A sustainable approach. *Renewable and Sustainable Energy Reviews* 158, 112130.
1082 <https://doi.org/10.1016/j.rser.2022.112130>
- 1083 97. Ravindran, R., Jaiswal, A.K., 2016. A comprehensive review on pre-treatment
1084 strategy for lignocellulosic food industry waste: Challenges and opportunities.

- 1085 Bioresource Technology 199, 92–102. <https://doi.org/10.1016/j.biortech.2015.07.106>
- 1086 98. Reddy, K., Nasr, M., Kumari, S., Kumar, S., Gupta, S.K., Enitan, A.M., Bux, F.,
1087 2017. Biohydrogen production from sugarcane bagasse hydrolysate: effects of pH,
1088 S/X, Fe²⁺, and magnetite nanoparticles. Environmental Science and Pollution
1089 Research 24, 8790–8804. <https://doi.org/10.1007/s11356-017-8560-1>
- 1090 99. Ren, N.Q., Guo, W.Q., Wang, X.J., Xiang, W.S., Liu, B.F., Wang, X.Z., Ding, J.,
1091 Chen, Z.B., 2008. Effects of different pretreatment methods on fermentation types and
1092 dominant bacteria for hydrogen production. International Journal of Hydrogen Energy
1093 33, 4318–4324. <https://doi.org/10.1016/j.ijhydene.2008.06.003>
- 1094 100. Rossi, D.M., Berne Da Costa, J., Aquino De Souza, E., Peralba, M.D.C.R.,
1095 Samios, D., Záchia Ayub, M.A., 2011. Comparison of different pretreatment methods
1096 for hydrogen production using environmental microbial consortia on residual glycerol
1097 from biodiesel. International Journal of Hydrogen Energy 36, 4814–4819.
1098 <https://doi.org/10.1016/j.ijhydene.2011.01.005>
- 1099 101. Sahoo, D., Ummalya, S.B., Okram, A.K., Pandey, A., Sankar, M.,
1100 Sukumaran, R.K., 2018. Effect of dilute acid pretreatment of wild rice grass (*Zizania*
1101 *latifolia*) from Loktak Lake for enzymatic hydrolysis. Bioresource Technology 253,
1102 252–255. <https://doi.org/10.1016/j.biortech.2018.01.048>
- 1103 102. Sarkar, O., Rova, U., Christakopoulos, P., Matsakas, L., 2022. Organosolv
1104 pretreated birch sawdust for the production of green hydrogen and renewable
1105 chemicals in an integrated biorefinery approach. Bioresource Technology 344,
1106 126164. <https://doi.org/10.1016/j.biortech.2021.126164>
- 1107 103. Shah, T.A., Tabassum, R., 2018. Enhancing biogas production from lime
1108 soaked corn cob residue. International Journal of Renewable Energy Research 8, 761–
1109 766. <https://doi.org/10.20508/ijrer.v8i2.7254.g7365>
- 1110 104. Shen, J., Zhao, C., Liu, G., Chen, C., 2017. Enhancing the Performance on
1111 Anaerobic Digestion of Vinegar Residue by Sodium Hydroxide Pretreatment. Waste
1112 and Biomass Valorization 8, 1119–1126. <https://doi.org/10.1007/s12649-016-9666-2>
- 1113 105. Shirkavand, E., Baroutian, S., Gapes, D.J., Young, B.R., 2016. Combination
1114 of fungal and physicochemical processes for lignocellulosic biomass pretreatment - A
1115 review. Renewable and Sustainable Energy Reviews 54, 217–234.
1116 <https://doi.org/10.1016/j.rser.2015.10.003>
- 1117 106. Silva, T.L. da, Reis, A., 2016. Algal biorefinery: An integrated approach, in:

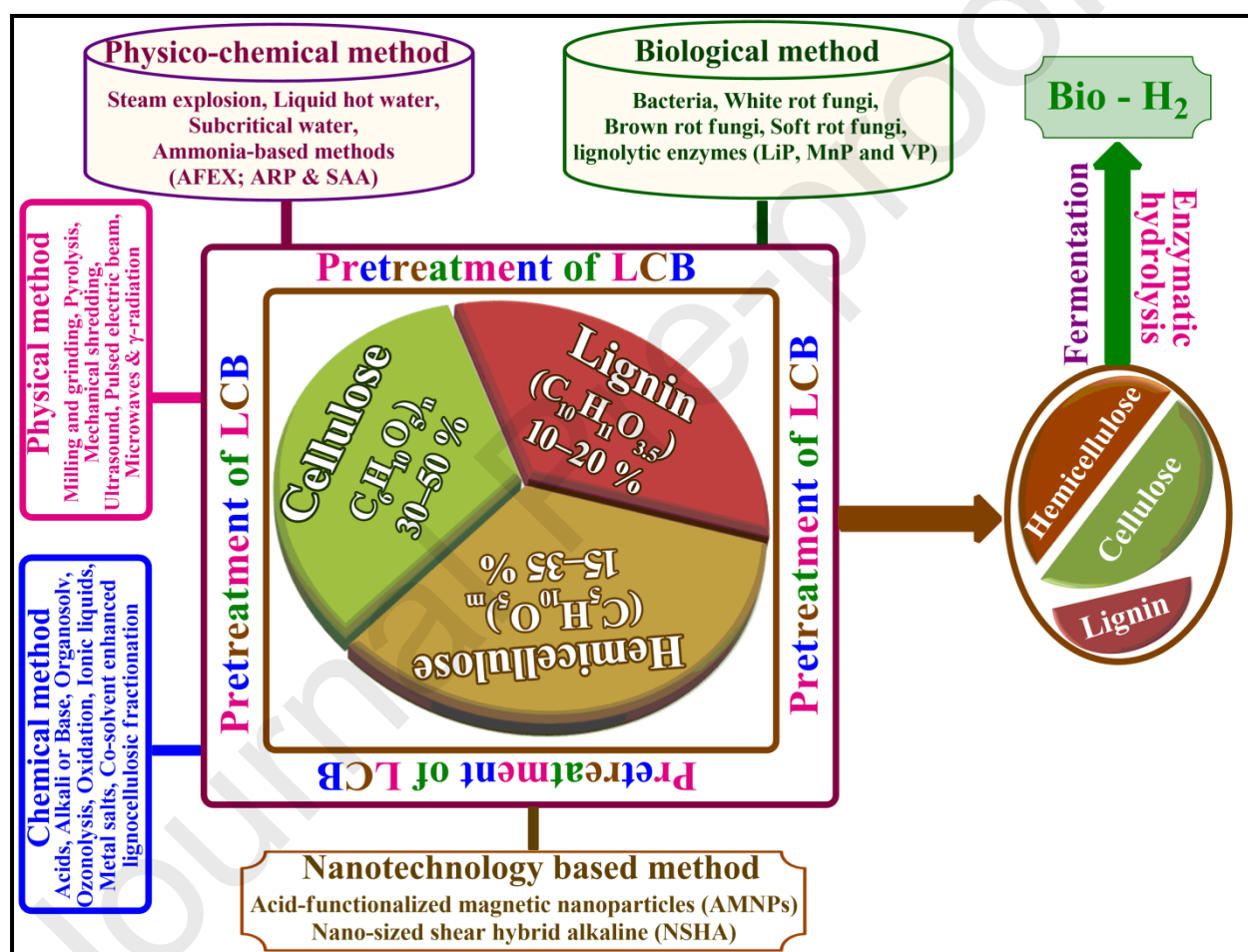
- 1118 Algal Biorefinery: An Integrated Approach. pp. 1–467. <https://doi.org/10.1007/978-3->
1119 319-22813-6
- 1120 107. Silverstein, R.A., Chen, Y., Sharma-Shivappa, R.R., Boyette, M.D., Osborne,
1121 J., 2007. A comparison of chemical pretreatment methods for improving
1122 saccharification of cotton stalks. *Bioresource Technology* 98, 3000–3011.
1123 <https://doi.org/10.1016/j.biortech.2006.10.022>
- 1124 108. Singh, H., Tomar, S., Qureshi, K.A., Jaremko, M., Rai, P.K., 2022. Recent
1125 Advances in Biomass Pretreatment Technologies for Biohydrogen Production.
1126 *Energies* 15, 1–22. <https://doi.org/10.3390/en15030999>
- 1127 109. Singh, J.K., Sharma, R.K., Ghosh, P., Kumar, A., Khan, M.L., 2018.
1128 Imidazolium Based Ionic Liquids: A Promising Green Solvent for Water Hyacinth
1129 Biomass Deconstruction. *Frontiers in Chemistry* 6, 548.
1130 <https://doi.org/10.3389/fchem.2018.00548>
- 1131 110. Singhvi, M., Kim, B.S., 2020. Current Developments in Lignocellulosic
1132 Biomass Conversion into Biofuels Using Nanobiotechnology Approach. *Energies* 13,
1133 5300. <https://doi.org/10.3390/en13205300>
- 1134 111. Sinha, P., Pandey, A., 2011. An evaluative report and challenges for
1135 fermentative biohydrogen production. *International Journal of Hydrogen Energy* 36,
1136 7460–7478. <https://doi.org/10.1016/j.ijhydene.2011.03.077>
- 1137 112. Solarte-Toro, J.C., Romero-García, J.M., Martínez-Patiño, J.C., Ruiz-Ramos,
1138 E., Castro-Galiano, E., Cardona-Alzate, C.A., 2019. Acid pretreatment of
1139 lignocellulosic biomass for energy vectors production: A review focused on
1140 operational conditions and techno-economic assessment for bioethanol production.
1141 *Renewable and Sustainable Energy Reviews* 107, 587–601.
1142 <https://doi.org/10.1016/j.rser.2019.02.024>
- 1143 113. Suhara, H., Kodama, S., Kamei, I., Maekawa, N., Meguro, S., 2012. Screening
1144 of selective lignin-degrading basidiomycetes and biological pretreatment for
1145 enzymatic hydrolysis of bamboo culms. *International Biodeterioration and*
1146 *Biodegradation* 75, 176–180. <https://doi.org/10.1016/j.ibiod.2012.05.042>
- 1147 114. Sun, Y., Cheng, J., 2002. Hydrolysis of lignocellulosic materials for ethanol
1148 production: A review. *Bioresource Technology* 83, 1–11.
1149 [https://doi.org/10.1016/S0960-8524\(01\)00212-7](https://doi.org/10.1016/S0960-8524(01)00212-7)
- 1150 115. Taherdanak, M., Zilouei, H., Karimi, K., 2016. The effects of Fe₀ and Ni₀

- 1151 nanoparticles versus Fe²⁺ and Ni²⁺ ions on dark hydrogen fermentation.
1152 International Journal of Hydrogen Energy 41, 167–173.
1153 <https://doi.org/10.1016/j.ijhydene.2015.11.110>
- 1154 116. Testa, M.L., Tummino, M.L., 2021. Lignocellulose biomass as a
1155 multifunctional tool for sustainable catalysis and chemicals: An overview. Catalysts
1156 11, 1–27. <https://doi.org/10.3390/catal11010125>
- 1157 117. Trinh, T.N., Jensen, P.A., Sárossy, Z., Dam-Johansen, K., Knudsen, N.O.,
1158 Sørensen, H.R., Egsgaard, H., 2013. Fast pyrolysis of lignin using a pyrolysis
1159 centrifuge reactor. Energy and Fuels 27, 3802–3810.
1160 <https://doi.org/10.1021/ef400527k>
- 1161 118. Usmani, Z., Sharma, M., Gupta, P., Karpichev, Y., Gathergood, N., Bhat, R.,
1162 Gupta, V.K., 2020. Ionic liquid based pretreatment of lignocellulosic biomass for
1163 enhanced bioconversion. Bioresource Technology 304, 123003.
1164 <https://doi.org/10.1016/j.biortech.2020.123003>
- 1165 119. Venkata Mohan, S., Lalit Babu, V., Sarma, P.N., 2008. Effect of various
1166 pretreatment methods on anaerobic mixed microflora to enhance biohydrogen
1167 production utilizing dairy wastewater as substrate. Bioresource Technology 99, 59–
1168 67. <https://doi.org/10.1016/j.biortech.2006.12.004>
- 1169 120. Vivekanand, V., Olsen, E.F., Eijsink, V.G.H., Horn, S.J., 2014. Methane
1170 Potential and Enzymatic Saccharification of Steam-exploded Bagasse. BioResources
1171 9, 1311–1324. <https://doi.org/10.15376/biores.9.1.1311-1324>
- 1172 121. Vu, H.P., Nguyen, L.N., Vu, M.T., Jahir, M.A.H., McLaughlan, R., Nghiem,
1173 L.D., 2020. A comprehensive review on the framework to valorise lignocellulosic
1174 biomass as biorefinery feedstocks. Science of the Total Environment 743, 140630.
1175 <https://doi.org/10.1016/j.scitotenv.2020.140630>
- 1176 122. Wang, J., Qian, Y., Li, L., Qiu, X., 2020. Atomic Force Microscopy and
1177 Molecular Dynamics Simulations for Study of Lignin Solution Self-Assembly
1178 Mechanisms in Organic–Aqueous Solvent Mixtures. ChemSusChem 13, 4420–4427.
1179 <https://doi.org/10.1002/cssc.201903132>
- 1180 123. Wang, J., Wan, W., 2008. Comparison of different pretreatment methods for
1181 enriching hydrogen-producing bacteria from digested sludge. International Journal of
1182 Hydrogen Energy 33, 2934–2941. <https://doi.org/10.1016/j.ijhydene.2008.03.048>
- 1183 124. Wang, N., Zhang, J., Wang, H., Li, Q., Wei, S., Wang, D., 2014. Effects of

- 1184 metal ions on the hydrolysis of bamboo biomass in 1-butyl-3-methylimidazolium
1185 chloride with dilute acid as catalyst. *Bioresource Technology* 173, 399–405.
1186 <https://doi.org/10.1016/j.biortech.2014.09.125>
- 1187 125. Wimonsong, P., Nitorisavut, R., 2015. Comparison of Different Catalysts for
1188 Fermentative Hydrogen Production. *Journal of Clean Energy Technologies* 3, 128–
1189 131. <https://doi.org/10.7763/jocet.2015.v3.181>
- 1190 126. Wimonsong, P., Nitorisavut, R., 2014. Biohydrogen enhancement using highly
1191 porous activated carbon. *Energy and Fuels* 28, 4554–4559.
1192 <https://doi.org/10.1021/ef500530v>
- 1193 127. Yang, G., Wang, J., 2018. Improving mechanisms of biohydrogen production
1194 from grass using zero-valent iron nanoparticles. *Bioresource Technology* 266, 413–
1195 420. <https://doi.org/10.1016/j.biortech.2018.07.004>
- 1196 128. Yin, Y., Hu, J., Wang, J., 2014. Enriching hydrogen-producing bacteria from
1197 digested sludge by different pretreatment methods. *International Journal of Hydrogen*
1198 *Energy* 39, 13550–13556. <https://doi.org/10.1016/j.ijhydene.2014.01.145>
- 1199 129. Yoo, C.G., Pu, Y., Ragauskas, A.J., 2017. Ionic liquids: Promising green
1200 solvents for lignocellulosic biomass utilization. *Current Opinion in Green and*
1201 *Sustainable Chemistry* 5, 5–11. <https://doi.org/10.1016/j.cogsc.2017.03.003>
- 1202 130. Yuan, Z., Wen, Y., Li, G., 2018. Production of bioethanol and value added
1203 compounds from wheat straw through combined alkaline/alkaline-peroxide
1204 pretreatment. *Bioresource Technology* 259, 228–236.
1205 <https://doi.org/10.1016/j.biortech.2018.03.044>
- 1206 131. Zhang, K., Ren, N., Guo, C., Wang, A., Cao, G., 2011. Effects of various
1207 pretreatment methods on mixed microflora to enhance biohydrogen production from
1208 corn stover hydrolysate. *Journal of Environmental Sciences* 23, 1929–1936.
1209 [https://doi.org/10.1016/S1001-0742\(10\)60679-1](https://doi.org/10.1016/S1001-0742(10)60679-1)
- 1210 132. Zhang Zhi-guo, 2012. Enhancement of the enzymatic hydrolysis of wheat
1211 straw by pretreatment with 1-allyl-3-methylimidazolium chloride ([Amim]Cl).
1212 *African Journal of Biotechnology* 11, 8032–8037. <https://doi.org/10.5897/ajb11.3583>
- 1213 133. Zhao, W., Zhang, Y., Du, B., Wei, D., Wei, Q., Zhao, Y., 2013. Enhancement
1214 effect of silver nanoparticles on fermentative biohydrogen production using mixed
1215 bacteria. *Bioresource Technology* 142, 240–245.
1216 <https://doi.org/10.1016/j.biortech.2013.05.042>

- 1217 134. Zheng, Y., Zhao, J., Xu, F., Li, Y., 2014. Pretreatment of lignocellulosic
1218 biomass for enhanced biogas production. Progress in Energy and Combustion Science
1219 42, 35–53. <https://doi.org/10.1016/j.peccs.2014.01.001>
- 1220 135. Zhu, J., Wan, C., Li, Y., 2010. Enhanced solid-state anaerobic digestion of
1221 corn stover by alkaline pretreatment. Bioresource Technology 101, 7523–7528.
1222 <https://doi.org/10.1016/j.biortech.2010.04.060>

Graphical Abstract



- 1226 136.

Highlights

- 1229 • Recent lignocellulosic pretreatments have been documented.
- 1230 • Radiation energy based pretreatment techniques were discussed.
- 1231 • Role of nanotechnology in bio-H₂ production has been highlighted
- 1232 • Challenges in the development of pretreatments and remedies are suggested.

1233

1234 137.

1235 **CRedit authorship contribution statement**

1236 Chyi-How Lay: Conceptualization, Writing – original draft & editing. Jeyaprakash

1237 Dharmaraja Conceptualization, Writing – original draft, review & editing. Sutha Shobana:

1238 Conceptualization, Writing – original draft, review & editing. Sundaram Arvindnarayan:

1239 Writing – review & editing. Retnam Krishna Priya: Writing – review & editing. Rajesh Banu

1240 J: Writing – review & editing. Young-kwon Park: Writing – review & editing. Vinod Kumar:

1241 Writing – review & editing, Rijuta Saratlae– Writing – review & editing, Gopalakrishnan

1242 Kumar: Writing – review & editing, Funding acquisition, Project administration &

1243 Supervision.

1244

1245 138.

Lignocellulose biohydrogen towards net zero emission: a review on recent developments

Laya, Chyi–How

2022-10-12

Attribution-NonCommercial-NoDerivatives 4.0 International

Lay CH, Dharmaraja J, Shobana S, et al., (2022) Lignocellulose biohydrogen towards net zero emission: a review on recent developments, *Bioresource Technology*, Volume 364, November 2022, Article number 128084

<https://doi.org/10.1016/j.biortech.2022.128084>

Downloaded from CERES Research Repository, Cranfield University