# 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.



## Bioresource Technology, Volume 364, November 2022, Article number 128084 DOI: 10.1016/j.biortech.2022.128084

- 1 Lignocellulose biohydrogen towards net zero emission: A review on recent developments
- 2 Chyi–How Lay<sup>1,#</sup>, Jeyaprakash Dharmaraja<sup>2,#</sup>, Sutha Shobana<sup>3</sup>, Sundaram Arvindnarayan<sup>4</sup>,
- 3 Retnam Krishna Priya<sup>5</sup>, Rajesh Banu J<sup>6</sup>, Rijuta Saratlae<sup>7</sup>, Young Kwon Park<sup>8</sup>, Vinod Kumar<sup>9</sup>,
- 4 Gopalakrishnan Kumar<sup>10\*</sup>
- 5
- 6 <sup>1</sup> Department of Environmental Engineering, Feng Chia University, Taichung, Taiwan
- <sup>7</sup> <sup>2</sup> Division of Chemistry, Faculty of Science and Humanities, AAA College of Engineering and
- 8 Technology, Amathur–626005, Virudhunagar District, Tamil Nadu, India.
- 9 <sup>3</sup> 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 <sup>4</sup>Department of Mechanical Engineering, Lord Jegannath College of Engineering and
- 12 Technology, Marungoor 629402, Kanyakumari District, Tamil Nadu, India.
- 13 <sup>5</sup>Research Department of Physics, Holy Cross College (Autonomous), Nagercoil 629004,
- 14 Kanyakumari District, Tamil Nadu, India.
- 15 <sup>6</sup>Department of Life Science, Central University of Tamilnadu, India
- <sup>7</sup>Research Institute of Integrative Life Sciences, Dongguk University-Seoul, Ilsandong-gu,
- 17 Goyang-si, Gyeonggido, 10326, Republic of Korea
- 18 <sup>8</sup>School of Environmental Engineering, University of Seoul, Seoul 02504, Republic of Korea
- <sup>9</sup>School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, United
- 20 Kingdom
- 21 <sup>10</sup>School of Civil and Environmental Engineering, Yonsei University, Seoul 03722, Republic of
- 22 Korea,
- 23
- 24 <sup>#</sup> Authors have equal contribution to this work.
- 25
- 26
- 27 \*Corresponding Author:
- 28 Gopalakrishnan Kumar, Email: gopalakrishnanchml@gmail.com
- 29

31	Abstract
32	This review mainly determines novel and advance physical, chemical, physico-chemical,
33	microbiological and nanotechnology-based pretreatment techniques in lignocellulosic biomass
34	pretreatment for bio-H2 production. Further, aim of this review is to gain the knowledge on the
35	lignocellulosic biomass pretreatment and its priority on the efficacy of bio-H2 and positive
36	findings. The influence of various pretreatment techniques on the structure of lignocellulosic
37	biomass have presented with the pros and cons, especially about the cellulose digestibility and
38	the interference by generation of inhibitory compounds in the bio-enzymatic technique as such
39	compounds is toxic. The result implies that the stepwise pretreatment technique only can ensure
40	eventually the lignocellulosic biomass materials fermentation to yield bio-H2. Though, the
41	mentioned pretreatment steps are still a challenge to procure cost-effective large-scale
42	conversion of lignocellulosic biomass into fermentable sugars along with low inhibitory
43	concentration.
44	
45	<i>Keywords:</i> Lignocellulosic biomass; bio $-H_2$ ; Pretreatment; Nanotechnology; Challenges.
46	
47	
48	
49 50	
51	
52	
53	
54	
55	
56	
57 58	
59	
60	
61	
62	

## 63 1. Introduction

The lignocelluloses have been originated from both the edible and non-edible industries 64 65 and are sustainable as well as promising materials for the productivity of second generation bio-66 fuels, which mainly include bio-ethanol, bio-H<sub>2</sub>, biogas, bio-methane, synthetic bio-fuels, biodiesel etc. Lignocellulosic biomass is a renewable resource and an interesting alternative for 67 68 fossil fuels since it consists of large amounts of energy as well as organic compounds. Further, lignocelluloses are a basic components of plant materials and has widely been utilized by 69 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 oil pressing, sawmills, sugar beets, sunflowers, waste paper industries and other waste fragments 76 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-H<sub>2</sub> that is procured from lignocelluloses via fermentation is an alternative to petro-derived fuel itself as it is eco- friendly since there is no 79 80 emission of GHGs (greenhouse gases), mainly CO<sub>2</sub> (carbon dioxide) while its combustion (Moreno and Dufour, 2013). Further, bio-H<sub>2</sub> is a basic molecule in a range of chemicals as well 81 82 as petro-chemical processes, like production of ammonia, integrated circuits and optical fibers, methanol, methane, nitrobenzene derived aniline from nitrobenzene, polymers syn-gas, 83 84 hydrogenation derived olefins, etc. Bio-H<sub>2</sub> 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-H<sub>2</sub> can crucially be generated with energetic 87 potentiality by means of gasification from coal & coke, reforming process of steam methane as well as water gas from crude oil derived hydrocarbons, electrolysis of water and water gas shift. 88 All such processes not only need a high input of electrical power and fossil fuels utilization but 89 90 also depletion of green environment by means of air pollution. So, bio-resources have been 91 considered for larger scale production of bio-H<sub>2</sub> (Goryunov et al., 2016). In such a way the biomasses can be an alternative option to produce sustainable bio-H<sub>2</sub> energy to achieve short-92

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 from the year of 2012. According to IEA (International Energy Academy), it occupies absolutely 96 97 1.5% of the generation of world electricity (Sun and Cheng, 2002). The lingo-cellulosic materials biorefinery yield nearly 48 % of the biomass-derived energy under favorable 98 99 circumstances (Sun and Cheng, 2002). The main by-products of bio-refineries apart from the 100 bio-H<sub>2</sub> 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-H<sub>2</sub> via fermentation is the formation sugar 107 intermediates during hydrolysis. Thereby, it requires a proper lignocellulosic pretreatment in 108 bio-H<sub>2</sub> 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-H<sub>2</sub> 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, physicochemical, microbiological and nanotechnology based pretreatment techniques towards 117 118 lignocellulosic biomass pretreatment for bio-H<sub>2</sub> 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 materials, consequently followed by reduction in size of the lignocellulosic particles. Thus, there 132 133 is a way to enrich the available surface areas for efficient reagent/enzymatic processes, which can obviously lead to effective conversion /degradation / digestibility of the complex 134 135 polysaccharides of the lignocellulosic materials into simple monomers and are easily 136 metabolizable / easily producing fermentable sugars to yield bio-H<sub>2</sub>. There is further conversion of valuable bio-H<sub>2</sub> while the hydrolytic process with low energy consumption, accompanied by 137 the formation of non-toxic enzyme inhibitors, etc (Abraham et al., 2020; Dharmaraja et al., 138 139 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 pretreatment techniques (Anu et al., 2020; Ashokkumar et al., 2022; Dharmaraja et al., 2019; 143 144 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- $H_2$  and a range of value added products, besides. 147

- 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-H<sub>2</sub> 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 biomass materials to about 70 °C. Physical methods for lignocellulosic complex structure 165 mainly include mechanical shredding (grinding via chipping, milling); steam explosion & 166 AFEX (Ammonia fiber/freeze expansion), pyrolysis, radiation energy-based microwaves, 167 168 pulsed electric field and ultrasound techniques.

169

# 170 3.1.1. Mechanical shredding and Pyrolysis

Mechanical shredding (grinding via chipping, milling) for soft biomass at a 171 172 temperature of about 50–70 °C) leads to rupture the lignocellulosic fibers and thereby reduces the period of time duration to digest the materials up to about 23–59% for further treatment to 173 174 yield fermentative bio-H<sub>2</sub> (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 towards the lignocellulosic pretreatment with no production of unwanted products that assists 177 178 simultaneously the downstream conversion and processing of the lignocellulosic components (Martin-Sampedro et al., 2012). Though such an overall mechanical pretreatment process is 179 180 energy-intensive and, thereby one should bring its application for a reasonable raise in the output of final energy only. Pyrolysis is an alternative pretreatment technique for biomass 181 182 materials but not to produce bio-H<sub>2</sub>, 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 disintegration of biomass materials. Such kind of decomposition begins at about 200 °C. 184

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 $-H_2$  after suitable fermentation of the 189 biomass. Microwaves applied can be suspended in an acidic (1%, 2% / 3% H<sub>2</sub>SO<sub>4</sub> (sulfuric

190 acid) or alkaline solution NaOH (sodium hydroxide) that results in an effective increase in the extent of delignification of about 12-30 % (Diaz et al., 2013; Singh et al., 2022). The 191 192 application of microwave radiation for 5 min on sugarcane bagasse with water (distilled), acid of phosphorus (H<sub>3</sub>PO<sub>3</sub>: pH=3.0) and glycerol of about 10 % indicates that 5.4 % (w/w) 193 194 fractions of lignin and 11.3 % (w/w) fractions of xylan are disintegrated. In addition, after 24 h of incubation the sugarcane bagasse can be treated with microwaves to achieve a high yield 195 196 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  $\gamma$  radiation possesses highly 197 penetrating power (Kortei and Wiafe-kwagyan, 2014; Singh et al., 2022). Thereby, it can be 198 199 applied to thick materials, and it results in the biomass degradation to overcome biomass 200 recalcitrance, followed by solubility increase and decrease in mechanical strength. 201 Conversely, this technique has not been applied in industrial scale, owing to its costs and 202 environmental as well as some safety issues. Among the non-thermal technologies pulsed 203 electric fields (PEF) is an emerging one though that has not been extensively studied. It is owing to the fact that the precise mechanisms by pulsed electric fields are not well 204 205 understood. However, to achieve many of these processes require very high treatment intensities, and duration from microseconds to milliseconds may cause temporary effects only 206 207 (Kortei and Wiafe-kwagyan, 2014; Singh et al., 2022). Moreover, inactivating pulsed electric 208 field is the safety measure as per the International guidelines and national safety standards for 209 electromagnetic fields, which are developed on the basis of the current scientific knowledge. 210 I-yrradiation has high potential, though its development and commercialization has been obstructed in the favor of public perceptions. Furthermore, the employment of ultrasonication 211 212 of frequency 20-40 kHz for biomass pretreatment obviously results in decomposition of the lignocellulosic biomass structures by means of loosening, swelling, and rupturing of fibrils 213 214 via breaking of inter molecular hydrogen linkages (Kucharska et al., 2018) for producing fermentative bio-H<sub>2</sub>, more effectively. Conversely, the economic viability on the 215 fermentation to yield bio-H<sub>2</sub> obviously can be led by mechanical pretreatment, correlated to 216 217 high energy operations for the mechanical biomass chipping fragmentation (Kucharska et al., 218 2018).

- 219
- 220
- 221
- 222

# 223 3.2. Chemical Pretreatment for Lignocellulosic Biomass

Generally, the chemical pretreatment for lignocellulosic biomass (LCB) materials processes are more widely utilized than other physical or biological methods, since, they are more effective as well as enhance the biodegradation of complex LCB materials to yield bio–H<sub>2</sub>. The common chemicals such as H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, HCOOH, CH<sub>3</sub>COOH, NaOH, KOH, Ca(OH)<sub>2</sub>, NH<sub>3(aqu)</sub>, H<sub>2</sub>O<sub>2</sub>, *etc.*, are widely utilized in this pretreatment process.

229

# 230 **3.2.1.** Acid pretreatment

In acid pretreatment method, when the lignocellulosic biomass materials are 231 pretreated with inorganic and organic acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, formic acid, 232 oxalic acid, maleic acid, etc., generate the hydrogen (H<sup>+</sup>) ions, which breakdown the 233 234 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 al., 2019). Generally, the acid pretreatment involves either the addition of concentrated acids 236  $(30-70\% \text{ at} < 100 \degree \text{C})$  or dilute acids (0.2 - 2.5 w/w% or 0.5 - 10% v/v at  $120 - 250 \degree \text{C})$  to 237 238 the LCB materials (Badiei et al., 2014). Dilute H<sub>2</sub>SO<sub>4</sub> pretreatment is commonly used for poplar, switch grass, spruce, and corn stover feedstocks. The conc. acid pretreatment can 239 240 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, aldehydes, 5-hydroxymethyl furfural and phenolic acids. Also, the recovery of acids after 243 244 hydrolysis process leads to the further treatment process (Amin et al., 2017). Hence, the effective acid pretreatment process involves the selection of acids as mild or dilute acids can 245 246 be utilized to breakdown the LCB materials into high conversion rate of sugar unit in an economical as well as environmental friendly manner with low generation of inhibitors 247 248 (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  $H_2SO_4$  (0.4 %) and NaOH (1 %) pretreatment on wild rice grass (Zizania latifolia) for enzymatic hydrolysis and showed 163 250 and 92 mg sugar g<sup>-1</sup> respectively. This study proves the dilute mineral acids pretreatment 251 process is more effective than alkali methods. Furthermore, the organic acids such as oxalic, 252 maleic, citric and formic acids are more efficient than dilute mineral acids for LCB 253 254 pretreatment for efficient industrial scale fermentative production of bio-H<sub>2</sub> (Baruah et al., 255 2018).

# 256 3.2.2. Alkaline pretreatment

Alkaline or base pretreatment involves the addition of alkaline reagents or bases (such 257 258 as NaOH, KOH, Ca(OH)<sub>2</sub>, NH<sub>4</sub>OH, 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 salination as well as water pollution (Kumari and Singh, 2018). Yuan et al. (Yuan et al., 268 2018), investigated the NaOH and Na<sub>2</sub>CO<sub>3</sub> pretreatments on wheat straw at 0 °C for 6 h and 269 showed a solid dissolution efficiency of 86.7 and 91.1 %, respectively. They also showed an 270 271 improved lignin solubilization as well as hydrolysis of cellulose and hemicellulose that obviously leads to increase the biogas generation. Shen et al., (Shen et al., 2017) reported that 272 NaOH pretreatment on vinegar residue (VR) showed an increased CH<sub>4</sub> yield (205.86 mL g<sup>-1</sup> 273 at 3% NaOH), that is 54 % higher than the untreated VR. Zhu et al., (Zhu et al., 2010) 274 275 reported that over 37 % of biogas can be produced from corn stover by NaOH pretreatment than untreated ones. Shah and Tabassum (Shah and Tabassum, 2018) investigated the lime 276 277 [Ca(OH)<sub>2</sub>] pretreatment on corn cob residue accelerates the digestion process followed by removal of lignin and enhances the biogas productions to 2 times higher than the untreated 278 279 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 liquor and high energy input for hydrolysis (Ashokkumar et al., 2022; Shirkavand et al., 282 2016; Vu et al., 2020). Effects of acidic and alkaline pretreatments on bio-H<sub>2</sub> production are 283 284 given in Table 1.

285

- 287
- 288

Table 1. Effects of acid and alkali on bio-H<sub>2</sub> production through inoculum pretreatment [Adopted from modified Ref. (Bundhoo et al., 2015)].

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

		With Pre-acidification (10 M HCl)	
		Control: 32.6 ml	
		Treated: 320.2 ml	
		Yield : + 882.20 %	
Sludge	Substrate: Glucose	Control: 0.7 mol mol <sup>-1</sup> glucose	(Elbeshbishy et al., 2010)
	Acid: 1 N HCl	Treated: 1.11 mol mol <sup>-1</sup> glucose	
	pH: 3.0 (24 h, 4 °C)	Yield : + 58.60 %	
	Substrate: Glucose	Control: 0.7 mol mol <sup>-1</sup> glucose	
	Alkali: 1 N NaOH	Treated: 0.68 mol mol <sup>-1</sup> glucose	
	pH: 10.0 (24 h, 4 °C)	Yield : - 2.90%	
	Substrate: Corn stover hydrolysate	Control: 2.7 mmol g <sup>-1</sup> sugar used	(Zhang et al., 2011)
	Acid: 1.0 M HCl	Treated: 3.21 mmol g <sup>-1</sup> sugar used	
	pH: 3.0 (24 h)	Yield : + 18.90 %	
	Substrate: Corn stover hydrolysate	Control: 2.7 mmol mmol g <sup>-1</sup> sugar <sub>used</sub>	
	Alkali: 1.0 M NaOH	Treated: 4.45 mmol mmol g <sup>-1</sup> sugar <sub>used</sub>	
	pH: 12.0 (24 h)	Yield : + 64.80 %	
Methanogenic granules	Substrate: Glucose	Control: 0.42 ml g <sup>-1</sup> glucose	(Hu and Chen, 2007)
	Acid: 0.1 N HCl	Treated: 0.00 ml g <sup>-1</sup> glucose	
	pH: 3.0 (24 h)	Yield : - 100.00 %	
Sewage sludge	Substrate: Glucose	Control: 124.99 ml g <sup>-1</sup> glucose	(Hu and Chen, 2007)
	3	12	

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

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

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

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

	synthesis	Treated: 0.03 % mol g <sup>-1</sup> glycerol	
	Alkali: 1.0 M NaOH	Yield : - 97.50 %	
	pH: 10.0 (24 h)		
Anaerobic mixed	Substrate: Dairy wastewater	Control: 0.0018 mmol g <sup>-1</sup> COD	(Venkata Mohan et al.,
microflora	Acid: H <sub>3</sub> PO <sub>4</sub>	Treated: 0.0079 mmol g <sup>-1</sup> COD	2008)
	pH: 3.0 (24 h)	Yield : + 338.90 %	
Digested sludge	Substrate: Glucose	Control: 65.7 ml	(Wang and Wan, 2008)
	Acid: 1.0 M HCl	Treated: 96.8 ml	
	pH: 3.0 (24 h)	Yield : + 47.30 %	
	Substrate: Glucose	Control: 65.7 ml	
	Alkali: 1.0 M NaOH	Treated: 125.9 ml	
	pH: 10.0 (24 h)	Yield : + 91.60 %	
292			
293			
294			
295			
296			
297			

# 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<sub>2</sub>SO<sub>4</sub>, 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 solid (Amiri et al., 2014). In general, lower EtOH / H<sub>2</sub>O ratios favor the hemicellulose 313 hydrolysis and enzymatic degradability of pretreated LCB since EtOH inhibits the 314 performance of hydrolytic enzymes. The ethanosolv pretreatment with H<sub>2</sub>SO<sub>4</sub> on 315 saccharification of poplar biomass has released upto 78 % of the polysaccharides (Chu et al., 316 2021). Koo et al., (Koo et al., 2011) investigated the aqueous EtOH (50 % v/v) with 1 % 317 318 NaOH on Liriodendron tulipifera (Tullip 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<sub>2</sub>SO<sub>4</sub> (w/w biomass). The 322 pretreated contents then were separated by means of vacuum filtration from the slurry. Consequently, washed with 1.1 L 60% of v/v ethanol/water mixture and finally dried in an 323 324 oven at 50 °C, overnight. The collected filtrate was used to produce acidogenic fermentative green bio-H<sub>2</sub> (121.4 mL/gVS) (Sarkar et al., 2022). By comparing with other pretreatments, 325 organosolv pretreatment process has many advantages such as ease of recovery of solvents by 326 distillation, low environmental impact, and recovery of high quality lignin as high value 327 328 added by-product.

329

# 330 3.2.4. Ozonolysis pretreatment

In this pretreatment method, the powerful oxidant say ozone (O<sub>3</sub>) is sparged into LCB materials, the lignin and hemicellulose contents are degraded but the cellulose fraction is not 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 O<sub>3</sub> 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 than the others. García-Cubero et al., (García-Cubero et al., 2009) reported the improved 342 enzymatic hydrolysis yields of wheat and rye straw upto 89% and 57% respectively, while 343 for the untreated wheat and rye straw the enzymatic hydrolysis yields were 29 % and 16 % 344 345 respectively.

346

## 347

## 3.2.5. Oxidation pretreatment

In this method, the powerful oxidizing agents like hydrogen peroxide  $(H_2O_2)$  or 348 alcoholic solution of peracidic acid are widely being employed for the pretreatment of LCB 349 materials i.e., the oxidant completely dissolves the lignin and amorphous cellulose, while 350 351 hemicellulose fractions undergo dissolution but the crystalline cellulose content is not dissolved in it (Kucharska et al., 2018). The LCB materials with H<sub>2</sub>O<sub>2</sub> generate •OH radicals, 352 which vigorously oxidize as well as degrade lignin fraction. The optimal dosage of H<sub>2</sub>O<sub>2</sub> is 353 2.15 % (v/v) at 35 °C and showed effective hydrolysis of LCB materials (Kucharska et al., 354 2018). The wet oxidation pretreatment of lignocellulosic biomass is done at 195 °C for 10–20 355 min (Anu et al., 2020) with the help of an oxidizer. This pretreatment method is a rapid and 356 357 effective processes but the formation of inhibitors during fermentation process is its main demerit. The whole hemicellulose and  $\sim 50$  % of lignin fractions present in the LCB materials 358 359 have been solubilized by treatment with  $1-2 \% H_2O_2$  at temperature of 25-30 °C. Pedersen and Meyer (Pedersen and Meyer, 2009) studied the pretreated of wheat straw with wet 360 361 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*)

and anions (such as acetate, chloride, bromide, sulphate, methanoate, nitrate, sulphate, 367 368 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 dissolution increases in presence of electron-withdrawing groups in the alkyl chains of IL 375 cations, hence, the cellulose moiety can undergo precipitation and the lignin can be dissolved 376 in ILs (Chen et al., 2017; Yoo et al., 2017). Some of the ILs like 1-ethyl-3-377 378 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-ethvl-3methylimidazoliumgroups, 1,3- dimethylimidazolium groups, cholinium amino acids, 381 382 cholinium acetate, 1-allyl-3-methylimidazolium chloride, etc., are widely utilized for the treatment of rice husk, water hyacinth, rice straw, kenaf powder, poplar wood, wheat straw, 383 384 and pine (Behera et al., 2014; Brandt et al., 2013; Kucharska et al., 2018; Shirkavand et al., 2016). The most popular IL is imidazolium-based salts namely Amimel (1-allyl-3-385 386 methylimidazolium chloride) and Bmimcl (1-butyl-3-methylimidazolium chloride), which may be effectively applied for cellulose dissolution when the temperature is < 100 °C (Baruah 387 388 et al., 2018; Kucharska et al., 2018). Zhi-Guo and Hong-Zhang (Zhang Zhi-guo, 2012) studied the pretreatment of wheat straw with Amim-Cl and showed 100 % increase in 389 glucose yield, when the temperature was increased from 125 to 150 °C at 2 h. Das et al., (Das 390 et al., 2021) reported the enzymatic hydrolysis and ethanol fermentation of several wood 391 392 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][HSO<sub>4</sub>] 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 ZnCl<sub>2</sub>, 403 FeCl<sub>3</sub>, FeCl<sub>2</sub>, CrCl<sub>2</sub>, MnCl<sub>2</sub>, AlCl<sub>3</sub>, 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 are removed by superfine filtration process. Chen et al., (Chen et al., 2014) studied the 405 406 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 moieties are degraded in the acid environment and a major share of them can be appeared in 408 the effluent. Wang et al., (Wang et al., 2014) investigated the hydrolysis of bamboo biomass 409 by dil. HCl in the presence of 1-butyl-3-methylimidazolium chloride with Cu<sup>2+</sup> ion showed a 410 411 maximum sugar yield of 67.1 % at 100 °C.

412

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

In this CELF method, a mixture of tetrahydrofuran (THF) and H<sub>2</sub>O is utilized as a monophasic solvent system. This pretreatment process involves the delignification followed by conversion of glucose-rich LCB materials into high value-added fuels, including 5– hydroxymethyl furfural (5–HMF), furfural and levulinic acid (LA) (Ashokkumar et al., 2022). Patri et al., 2021 (Patri et al., 2021) studied the THF co–solvent with mineral H<sub>2</sub>SO<sub>4</sub> (act as catalyst) on enzymatic hydrolysis of switchgrass biomass, yielded approximately 90 % glucose at 160 °C.

# 421

# 422 3.3. Physico-chemical pretreatment

423 Among physico-chemical pretreatments such as steam explosion (SE), liquid hot water (LHW), subcritical water (SCW) and ammonia-based methods are promising to 424 425 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 enzymes as well as fermentative microorganisms (Anu et al., 2020; Ravindran and Jaiswal, 428 429 2016). The steam explosion (SE) or autohydrolysis is one of the oldest and effective methods for enzymatic hydrolysis of LCB materials; the LCB materials are pretreated to a high steam 430 431 pressure (0.7-4.8 MPa) and temperature (160-206 °C) for 1-20 min. At very high temperature and pressure, the steam explosion as well as AFEX (ammonia fiber explosion) 432

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 explosion is the partial degradation of hemicelluloses and thereby producing toxic products. 435 436 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 (Baral and Shah, 2017) reported the steam explosion pretreatment of corn stover to produce 438 439 113.5 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 yield, up to 86 % was achieved at experimental conditions (Temp.: 201 °C, Pressure: 0.86 441 MPa; Time: 15 min). Vivekanand et al., (Vivekanand et al., 2014) reported the combined 442 sequential SO<sub>2</sub> with steam explosion methods, followed by enzymatic hydrolysis that showed 443 more effective polysaccharide conversion upto of 81 %. The LHW pretreatment is an ideal 444 445 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 formation of toxic components (Jiang et al., 2015; Ravindran and Jaiswal, 2016). Muharja et 449 450 al. (Muharja et al., 2018) studied the combined green process of subcritical water (SCW) and 451 enzymatic hydrolysis for bio-H<sub>2</sub> fermentation from coconut husk and the maximum bio-H<sub>2</sub> 452 yield, up to 0.279 mol/mol by consumption of sugar, which is lower than the other works. Further, ammonia (NH<sub>3</sub>) is an effective agent for the pretreatment of LCB materials. There 453 454 are three different ammonia-based methods namely (i) ammonia fiber explosion (AFEX), (ii) ammonia recycled percolation (ARP) and (iii) soaking aqueous ammonia (SAA). The AFEX 455 456 method is a novel advancement technology for the production of fermentable simple sugar units from LCB materials over conventional alkaline processes (Naik et al., 2021; Raj et al., 457 458 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 employed for low-lignin LCB materials like switchgrass, corn stover, Miscanthus, etc., 460 showed > 90 % of glucose yield, during simultaneous saccharification and fermentation 461 462 process. After the completion of pretreatment, the vaporized NH<sub>3</sub> has been collected, recycled and reused again. Jin et al (Jin et al., 2016) reported that the Great Lakes Bioenergy 463 464 Laboratories in the US have demonstrated the AFEX pretreatment method for cellulosic ethanol production, which reduced enzyme loading by 66 % and also increased EtOH 465

productivity by 129 %. In an ARP pretreatment process, the poplar wood is soaked in 15 %
of NH<sub>3 (aqu.)</sub> for 1 h at 40 °C and the pressure was increased to 20 bar. After increasing the
temperature upto 180 °C, more liquid extracting was percolated at the rate of 3 ml/min for 90
min. In this ARP method, the removal of lignin has been achieved 87 % (Naik et al., 2021).
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, decreases in the dependence on chemicals, etc., but main disadvantage is the low hydrolysis 475 rate. During the biological pretreatment of LCB materials, the microorganisms such as 476 477 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, such as brown, white, and soft rot fungi have widely been utilized to degrade the LCB 480 materials to produce fermentative bio-H<sub>2</sub> (Dey et al., 2022; Hassan et al., 2018). Certain 481 microorganisms are present in nature, which exhibit cellulolytic and hemicellulolytic 482 483 abilities. White rot is able to degrade lignin moieties, present in the LCB materials, which is due to the presence of lignin degrading enzymes like peroxidases and laccases. Brown rot 484 485 commonly attacks the cellulose content, whereas white as well as soft rot target both lignin and cellulose contents of LCB. Furthermore, the soft rot fungi are efficiently degrading the 486 487 wood polysaccharides however; the alteration of lignin is limited extent only. The commonly utilized white rot fungi like Cyathus stercoreus, Phanerochaete chrysosporium, Pleurotus 488 489 ostreatus, Ceriporiopsis subvermispora, Ceriporia lacerata, Pycnoporus cinnabarinus, 490 Cvathus stercolerus. Cvathus cinnabarinus. Ceriporia lacerata. Ceriporiopsis 491 subvermispora, Pvcnoporus 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 lignocellulosic materials (Peng et al., 2012). The degradation of lignin by lignolytic enzymes, 496 497 such as lignin peroxidase, manganese peroxidase and versatile peroxidase, are generated from various microorganisms, which also degrading the lignin structure completely by increasing 498

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 glucose/kg of dry rice straw. Recently, the isolated thermophilic 371.91 g 505 Thermoanaerobacterium sp. strain F6 produced 1822.6 and 826.3 mL H<sub>2</sub>/L of hydrogen 506 using corn cob and sugarcane bagasse respectively (Jiang et al., 2019).

507

# 508 3.5. Nanotechnical pretreatment

Nanotechnology-based pretreatment on lignocellulosic biomass structures is an 509 510 important methodology to yield bio-H<sub>2</sub>. 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. The AMNPs utilization to enzymatic immobilization, functionalization by means of 513 microbes/chemicals is an alternative to the traditional pretreatment techniques for 514 lignocellulosic biomass. Reusable nature of AMNPs and enzymes obviously is the cost-515 516 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 molecules to generate carbohydrates (Abdul Razack et al., 2016; Amin et al., 2017). 519

520

# 521 3.5.1. AMNPs pretreatment

AMNPs possess higher affinity for hydrolyzed lignocellulosic biomass materials, these are also named as solid acid nanocatalysts. Their reusability with strong magnetic nature has added beneficial role in chemical techniques (Peña et al., 2014). By the year of 2011, sulfonated MNPs were synthesized to hydrolyse the lignocellulosic biomass structure. Similarly, such functionalized MNPs significantly possess better stability and enhance the 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 shearing531 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 saccharification and refineries. Functionalization of NSHA system can be enhanced with 533 certain additives namely PDAC [Poly(diallyldimethylammonium chloride)] and are utilized 534 535 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- $H_2$ 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 be performed by metal nano particles (NPs) like Ni(nickel)/Fe(iron) materials. These nano-545 materials can act as cofactors (like hydrogenase), consequently reduces the exchange of 546 H<sup>(+)</sup>(protons) (Dey et al., 2022). The function of the microbes has been greatly influenced by 547 increasing the metal NPs concentration to yield bio-H. Such a nano-approach improves the 548 rate of e<sup>(-)</sup>(electron) transfer that suitably improves the metabolic activity of the micro–biota. 549 It has also been demonstrated that the metal NPs can improve the production of bio-H<sub>2</sub> in 550 551 acidic pH, moreover the substrate concentration increases with decrease of bio-H<sub>2</sub> production, *i.e.*, inverse effect. It was found that the metal oxide NPs can increase 4.5 times 552 553 of the bio-H<sub>2</sub> production, as compared to normal synthetic processes. Similar way with iron NPs (0.2 g/L), nearly a 33% increase in the bio-H<sub>2</sub> production was observed in sugar 554 555 (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-H<sub>2</sub> production by means of nano-material is still not 558 known clearly (Dey et al., 2022). Further, the main disadvantage of valuable nano-materials assisted technique is its slow rate of yield. It was found that nearly about 35% of 559 lignocellulosic components only converted effectively to bio-H<sub>2</sub> and the residues produce 560 some other by-products. Thereby, there a necessity is to upgrade the technique for industrial 561 production of bio-H<sub>2</sub> by lignocellulosic substrates via improvement/introduction of suitable 562 563 strain as well as nano-materials.

	Journal Pre-pi	roofs	
565 Table 2.	Production of bio-H <sub>2</sub> by NPs from	lignocellulosic mat	erials (Adopted
566	and modified from Ref. (Dey et al.,	2022).	
567			
Nanomaterials	Microbes / Natural substrate or	Bio-Hydrogen	References
	enzyme used	production	
	Enterobacter sp. and Clostridium sp. /	80.70 ml / h,	(Yang and Wang, 2018)
	Grass	73.10 %	
	Mesophilic culture / Starch	200.00 %	(Taherdanak et al., 2016)
	Anaerobic sludge / Sugarcane bagasse	69.00 %	(Reddy et al., 2017)
	Enterobacter aerogenes / Cassava	92.00 %	(Lin et al., 2016)
	starch		
	Anaerobic sludge bacteria / Molasses	43.00 %	(Gadhe et al., 2015)
Iron	waste		
	Thermophillic anaerobic mixed	53.60 %	(Engliman et al., 2017)
	culture / Glucose		
	Anaerobic mixed bacteria / Glucose	33.70 %	(C. Jia et al., 2017;
			J. Jia et al., 2017)
	Enterobacter cloacae / Glucose	130.00 %	(Nath et al., 2015)
	Clostridium butyricum / Sucrose	32.64 %	(Han et al., 2011)
	Rhodobacter sphaeroides / malate	19.40 %	(Bao et al., 2013)
	Bacillus anthracis / Palm oil mill	151.00 %	(Mishra et al., 2018)
	eluent		
Nickel	Anaerobic sludge bacteria / Molasses	24.00 %	(Gadhe et al., 2015;
	waste pH =5.6, T=30-35 °C with	22.00 %	Mullai et al., 2013)
	0.0567 wt % of Ni NPs / glucose	2.54 mol	
	Anaerobic mixed bacteria / Glucose	33.70 %	(C. Jia et al., 2017; J. Jia
	(Composite type of carbon)		et al., 2017)
	Anaerobic sludge/ Glucose (nanotube	50.00 %	(Singh et al., 2018)
Carbon	form of carbon)		
	Anaerobic sludge / Sucrose (activated	62.50 %	(Wimonsong and
	carbon)		Nitisoravut, 2015)
	Anaerobic sludge / Sucrose (nano	70.00 %	(Bhatia et al., 2021;

	Journal Pre-pro	oofs	
	activated carbon)		Wimonsong and
			Nitisoravut, 2014)
Noble metals	Silver NPs with Clostridium	67.50 %	(Zhao et al., 2013)
	<i>butyricum</i> / Glucose		
	Gold NPs with Anaerobic sludge /	—	(Khan et al., 2013)
	Acetate		
	Silver with Clostridium butyricum/	38.00 %	(Beckers et al., 2013;
	Glucose		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			

The outcomes of Table 2 in the view of production of  $bio-H_2$  by means of NPs and 569 570 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-H<sub>2</sub> yield by making high availability of active surface area with NPs for acceleration of reaction kinetics. Thereby, unwanted oxygen molecules can 573 574 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  $bio-H_2$  (73%) as 576 the main component for hydrogenase possibly was formed by such a nano system, since it has been associated with the enzymes ferredoxin as well as hydrogenase of the electron transport 577 Some other significant nano system has been formed by Ag(silver), Au(gold), 578 chain. Cu(copper), Pd(palladium), etc., to enhance production of bio-H<sub>2</sub> by means of dark 579 580 fermentation technique.

- 581
- 582

# 4. Research needs Perspectives and Future Directions

The physical pretreatment methods lead to reduce the size of lignocellulosic biomass components, cellulose crystalline index, and raise the availability of the catalytically active sites. This method includes the application of either mechanical shredding *via* grinding (milling and chipping), steam explosion, ammonia based pretreatments (AFEX) or radiation– based techniques *via* ultrasonication,  $\gamma$ , electron beam and microwave radiations (Mankar et al., 2021). In chemical pretreatment, the degradation/decomposition of lignocellulosic 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 industrial applications. Further, these pretreatment processes enhance the solubility of 598 hemicellulose and lignin content for destructuralization of lignocellulose moieties to improve 599 the accessible specific surface on lignocellulosic biomass for enzymes, while with certain 600 601 slight environmental impacts. The major physico-chemical pretreatment techniques consists 602 of EA: Extractive ammonia and SAA: Soaking aqueous ammonia, supercritical fluid:SCF like  $ScCO_2$ . Supercritical carbon dioxide:  $ScH_2O$ : Supercritical water and  $ScNH_3$ : 603 Supercritical ammonia explosion, liquid hot water :LHW, hydrothermolysis, uncatalyzed 604 605 solvolysis, aquasolv and aqueous fraction processes, microwave assisted chemcial and SPORL a sulfite pretreatment: (Sulfite pretreatment to overcome recalcitrance of 606 607 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 fermentable sugar moieties and their consequent conversion into high value added bioenergy 610 611 as well as by-products through various pretreatment approaches. Some of the pretreatment approaches have been utilized in large scale industrial stage, but till now some significant 612 613 challenges fall in the category of intensively energy requirement, low process efficiency, generation of toxic or environmentally hazardous wastes/inhibitors, perturbation in the 614 615 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 need of green solvents, low consumption of energy and chemicals, minimization of the water 618 619 usage, operation with reduced or small particle size, etc. The following factors are to be surely considered in order to make LCB (lignocellulose biomass) pretreatment processes 620 621 efficient as well as effective, they are (i) utilization of large sized LCB particles to minimize the energy application, (ii) operation at very high concentrations of LCB materials to reduce 622

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 chemical pretreatment process, the usage of catalysts (both acid, alkali or other chemicals), 625 626 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 recycling with water from consequent processing steps because another major challenges 632 633 (Janusz et al., 2020, 2017). The LCB pretreatment processes include mechanical processing, microwave irradiation processing, wet oxidation, ozonolysis, hot water and supercritical CO<sub>2</sub> 634 635 and H<sub>2</sub>O techniques, no catalysts or expensive chemicals are utilized. So there is no recovery of chemicals or compounds during the processing, but the above techniques need high 636 expensive reactor units (Balan, 2014). Till now, the challenge for the effective enzymatic 637 638 digestibility of LCB materials is unclear in biological pretreatment process, which is due to the employed complicated structural unit present in the microbes or enzymes. Hence, each 639 640 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 LCB pretreatment process overcomes the above challenges more efficiently and effectively 643 644 than the other technologies (Ponnusamy et al., 2019; Testa and Tummino, 2021).

Pretreatment steps for lignocellulosic biomass materials to fermentable sugars are a 645 646 challenge in the case of large-scale conversion for procuring cost-effective and competitive technically derived products along with very low inhibitory concentration. Agricultural 647 residues have been utilized for industrial bio-fuel production via steam explosion, as it is an 648 649 important technology. This steam explosion in a 50 m<sup>3</sup> industrial reactor with corn-stover was performed, to yield 80% of hemicelluloses and then by hydrolysis more than 90 % of 650 celluloses were recovered (Kucharska et al., 2018). Pretreatment with dil. acids is 651 652 encouraging the production of bio-fuels, as of the biomass possesses high efficiency for the conversion of most of the hemicelluloses into soluble sugars, whereas this process forms 653 654 furfural like inhibitors compounds. The efficacy of acid hydrolysis enhances the pretreatment via optimization of reaction conditions and certain operational parameters viz. dosage of acid, 655

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 the production of commercial bio-fuel. Techno-economic analysis has shown that the 658 659 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 of the biomass feed that integrates the advantage of the concern pretreatment technique. As 664 well, in turn the combination of such processes can considerably progress the effectiveness of 665 enzyme hydrolysis. Binod et al., (Binod et al., 2012) employed a combination of microwave-666 667 chemical (-acid and -alkali) pretreatment in place of conventional acid/alkaline pretreatment. The results reveal that the combined treatment enhances the fermentable sugar yield within a 668 short period of time duration. Lai et al., (Lai and Idris, 2016) has suggested low-energy 669 ultrasound-chemical (-alkali) pretreatment for the enhancement of biodegradable nature of 670 671 lignocellulosic biomass feed. The combination of Ionic liquid-ultrasound process on bagasse, using cholinium IL is biocompatible, showing 80 % of the cellulose and 72% of 672 673 hemicellulose saccharification along with a little inhibitory effect on enzyme cellulose activity (Ninomiya et al., 2015, 2012). The integration of bioprocesses for the industries to 674 675 achieve coherent energy efficiency mainly involves the partly bioconversion of spent cooking oil into bio-fuels/cellulose products. Due to the overall cost of production on the 676 677 lignocellulosic biomass biofuels by fermentation, the wastewater management has given to importance as the biorefinery stillage contains a range of dissolved and unutilized 678 fermentable sugars mainly lignin of about 74.1–79.0 wt. % of the total biomass (Trinh et al., 679 2013). Consequently, this lignin has been utilized for the production of high-value added 680 products/by direct combustion to supply sufficient energy for the industrial processes. In this 681 682 regard, fast pyrolysis is currently attracting the interest of researchers since it has the potentiality for the efficient conversion of lignin to high commercially value products like as 683 bio-oil, bio-char, etc. (Trinh et al., 2013). But for the production of gaseous bio-fuels 684 685 towards the industrial application, a specific approach is required to comprehensively analyze the overall operating costs. The production of biogas by anaerobic digestion usually is a 686 687 heat/energy generating integrated process. Thereby, integrated technologies for the production of bio-H<sub>2</sub> are taken into consideration because utilization of value added products 688

and energy that can be cogenerated, simultaneously as the pretreatment techniques of lignocellulosic biomass is performed before the saccharification, enzymatically. In the case of bio $-H_2$ , high cost and low yields along with comparatively low concentration of fermentation 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 and optimized mainly for bio-ethanol production (Kucharska et al., 2018). The pretreatment 703 704 technologies for improving production of bio-H<sub>2</sub> from the DF process can be categorized according to their pretreated inoculums/substrates. They can be classified into physical, 705 706 chemical, physico-chemical, biological and nano-technical pretreatments, based on the biomass used. Amongst, the dissimilar technologies reviewed, acid pretreatments are the 707 708 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 pretreatment that may eventually form inhibitory compounds thereby can decrease bio-H<sub>2</sub> 711 712 production. As a result, the research needs to find out the best technique for both the substrates and inoculums in industrial scale while a simultaneous consideration towards both 713 714 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 straw, etc., food wastes, sludge, and wastewater stream to yield maximum. It has been 716 717 concluded that among the various pretreatments investigated for such kind of wastes, 718 ultrasound, combined and biological pretreatments have been utilized/employed to procure positive results. 719

- 720
- 721

722	5. Conclusions
723	Effective pretreatment technologies for improving production of bio-H <sub>2</sub> 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. Bioresource Technology 344, 126195. https://doi.org/10.1016/j.biortech.2021.126195 763 9. Azbar, N., Çetinkaya Dokgöz, F.T., Keskin, T., Korkmaz, K.S., Syed, H.M., 2009. 764 765 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 10. Badiei, M., Asim, N., Jahim, J.M., Sopian, K., 2014. Comparison of Chemical 768 Pretreatment Methods for Cellulosic Biomass. APCBEE Procedia 9, 170-174. 769 770 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 biochemical pathway: A review. Energy Conversion and Management 52, 858-875. 775 776 https://doi.org/10.1016/j.enconman.2010.08.013 13. Banoth, C., Sunkar, B., Tondamanati, P.R., Bhukya, B., 2017. Improved 777 778 physicochemical pretreatment and enzymatic hydrolysis of rice straw for bioethanol 779 production by yeast fermentation. 3 Biotech 7. https://doi.org/10.1007/s13205-017-0980-6 780 781 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, 38-44. https://doi.org/10.1016/j.fuel.2013.04.063 783 784 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 Bioresource Technology 232, 331-343. corn stover. https://doi.org/10.1016/j.biortech.2017.02.068 787

- 16. Barbanera, M., Buratti, C., Cotana, F., Foschini, D., Lascaro, E., 2015. Effect of
  steam explosion pretreatment on sugar production by enzymatic hydrolysis of olive
  tree pruning. Energy Procedia 81, 146–154.
  https://doi.org/10.1016/j.egypro.2015.12.069
- 17. Baruah, J., Nath, B.K., Sharma, R., Kumar, S., Deka, R.C., Baruah, D.C., Kalita, E.,
  2018. Recent trends in the pretreatment of lignocellulosic biomass for value-added
  products. Frontiers in Energy Research 6, 1–19.
  https://doi.org/10.3389/fenrg.2018.00141
- 18. Beckers, L., Hiligsmann, S., Lambert, S.D., Heinrichs, B., Thonart, P., 2013.
  Improving effect of metal and oxide nanoparticles encapsulated in porous silica on
  fermentative biohydrogen production by Clostridium butyricum. Bioresource
  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
- 26. Chaganti, S.R., Kim, D.H., Lalman, J.A., 2012. Dark fermentative hydrogen
  production by mixed anaerobic cultures: Effect of inoculum treatment methods on
  hydrogen yield. Renewable Energy 48, 117–121.
  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
- 28. Chang, K.L., Thitikorn-amorn, J., Hsieh, J.F., Ou, B.M., Chen, S.H.,
  Ratanakhanokchai, K., Huang, P.J., Chen, S.T., 2011. Enhanced enzymatic
  conversion with freeze pretreatment of rice straw. Biomass and Bioenergy 35, 90–95.
  https://doi.org/10.1016/j.biombioe.2010.08.027
- 29. Chang, S., Li, J.Z., Liu, F., 2011. Evaluation of different pretreatment methods for
  preparing hydrogen-producing seed inocula from waste activated sludge. Renewable
  Energy 36, 1517–1522. https://doi.org/10.1016/j.renene.2010.11.023
- 30. Chauhan, P.S., 2020. Role of various bacterial enzymes in complete depolymerization
  of lignin: A review. Biocatalysis and Agricultural Biotechnology 23, 101498.
  https://doi.org/10.1016/j.bcab.2020.101498
- 31. Chen, H., Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., Han, S., 2017. A
  review on the pretreatment of lignocellulose for high-value chemicals. Fuel
  Processing Technology 160, 196–206. https://doi.org/10.1016/j.fuproc.2016.12.007
- 32. Chen, L., Chen, R., Fu, S., 2014. Preliminary exploration on pretreatment with metal
  chlorides and enzymatic hydrolysis of bagasse. Biomass and Bioenergy 71, 311–317.
  https://doi.org/10.1016/j.biombioe.2014.09.026
- 33. Cheong, D.Y., Hansen, C.L., 2006. Bacterial stress enrichment enhances anaerobic
  hydrogen production in cattle manure sludge. Applied Microbiology and
  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
- 35. Das, L., Achinivu, E.C., Barcelos, C.A., Sundstrom, E., Amer, B., Baidoo, E.E.K.,
  Simmons, B.A., Sun, N., Gladden, J.M., 2021. Deconstruction of Woody Biomass via
  Protic and Aprotic Ionic Liquid Pretreatment for Ethanol Production. ACS
  Sustainable Chemistry and Engineering 9, 4422–4432.
  https://doi.org/10.1021/acssuschemeng.0c07925
- 36. Dey, N., Kumar, G., Vickram, A.S., Mohan, M., Singhania, R.R., Patel, A.K., Dong,
  C.-D., Anbarasu, K., Thanigaivel, S., Ponnusamy, V.K., 2022. Nanotechnologyassisted production of value-added biopotent energy-yielding products from
  lignocellulosic biomass refinery A review. Bioresource Technology 344, 126171.
  https://doi.org/10.1016/j.biortech.2021.126171
- 37. Dharmaraja, J., Shobana, S., Arvindnarayan, S., Vadivel, M., Atabani, A.E.,
  Pugazhendhi, A., Kumar, G., 2019. Biobutanol from lignocellulosic biomass:
  Bioprocess strategies. Lignocellulosic Biomass to Liquid Biofuels 169–193.
  https://doi.org/10.1016/B978-0-12-815936-1.00005-8
- 38. Diaz, A., Le Toullec, J., Blandino, A., De Ory, I., Caro, I., 2013. Pretreatment of rice
  hulls with alkaline peroxide to enhance enzyme hydrolysis for ethanol production.
  Chemical Engineering Transactions 32, 949–954.
  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
- 40. Engliman, N.S., Abdul, P.M., Wu, S.Y., Jahim, J.M., 2017. Influence of iron (II)
  oxide nanoparticle on biohydrogen production in thermophilic mixed fermentation.
  International Journal of Hydrogen Energy 42, 27482–27493.
  https://doi.org/10.1016/j.ijhydene.2017.05.224
- 41. Gadhe, A., Sonawane, S.S., Varma, M.N., 2015. Enhancement effect of hematite and
  nickel nanoparticles on biohydrogen production from dairy wastewater. International
  Journal of Hydrogen Energy 40, 4502–4511.
  https://doi.org/10.1016/j.ijhydene.2015.02.046
- 42. García-Cubero, M.T., González-Benito, G., Indacoechea, I., Coca, M., Bolado, S.,
  2009. Effect of ozonolysis pretreatment on enzymatic digestibility of wheat and rye

	Journal Pre-proofs
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., Świderska-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., Świderska-Burek, U., Polak, J., Sulej, J., Jarosz-Wilkołazka,
	37

- A., Paszczyński, A., 2020. Laccase Properties, Physiological Functions, and
  Evolution. International Journal of Molecular Sciences 21, 966.
  https://doi.org/10.3390/ijms21030966
- 54. Jia, C., Chen, L., Shao, Z., Agarwal, U.P., Hu, L., Zhu, J.Y., 2017. Using a fully
  recyclable dicarboxylic acid for producing dispersible and thermally stable cellulose
  nanomaterials from different cellulosic sources. Cellulose 24, 2483–2498.
  https://doi.org/10.1007/s10570-017-1277-y
- 55. Jia, J., Zhang, W., Yang, Z., Yang, X., Wang, N., Yu, X., 2017. Novel magnetic
  cross-linked cellulase aggregates with a potential application in lignocellulosic
  biomass bioconversion. Molecules 22. https://doi.org/10.3390/molecules22020269
- 56. Jiang, W., Chang, S., Li, H., Oleskowicz-Popiel, P., Xu, J., 2015. Liquid hot water
  pretreatment on different parts of cotton stalk to facilitate ethanol production.
  Bioresource Technology 176, 175–180. https://doi.org/10.1016/j.biortech.2014.11.023
- 57. Jiang, Y., Lu, J., Lv, Y., Wu, R., Dong, W., Zhou, J., Jiang, M., Xin, F., 2019.
  Efficient hydrogen production from lignocellulosic feedstocks by a newly isolated
  thermophlic Thermoanaerobacterium sp. strain F6. International Journal of Hydrogen
  Energy 44, 14380–14386. https://doi.org/10.1016/j.ijhydene.2019.01.226
- 58. Jin, M., Da Costa Sousa, L., Schwartz, C., He, Y., Sarks, C., Gunawan, C., Balan, V.,
  Dale, B.E., 2016. Toward lower cost cellulosic biofuel production using ammonia
  based pretreatment technologies. Green Chemistry 18, 957–966.
  https://doi.org/10.1039/c5gc02433a
- 59. Karimi, K., Taherzadeh, M.J., 2016. A critical review of analytical methods in
  pretreatment of lignocelluloses: Composition, imaging, and crystallinity. Bioresource
  Technology 200, 1008–1018. https://doi.org/10.1016/j.biortech.2015.11.022
- 60. Khan, M.M., Lee, J., Cho, M.H., 2013. Electrochemically active biofilm mediated
  bio-hydrogen production catalyzed by positively charged gold nanoparticles.
  International Journal of Hydrogen Energy 38, 5243–5250.
  https://doi.org/10.1016/j.ijhydene.2013.02.080
- 61. Khan, M.U., Usman, M., Ashraf, M.A., Dutta, N., Luo, G., Zhang, S., 2022. A review
  of recent advancements in pretreatment techniques of lignocellulosic materials for
  biogas production: Opportunities and Limitations. Chemical Engineering Journal
  Advances 10, 100263. https://doi.org/10.1016/j.ceja.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
- 63. Koo, B.W., Kim, H.Y., Park, N., Lee, S.M., Yeo, H., Choi, I.G., 2011. Organosolv
  pretreatment of Liriodendron tulipifera and simultaneous saccharification and
  fermentation for bioethanol production. Biomass and Bioenergy 35, 1833–1840.
  https://doi.org/10.1016/j.biombioe.2011.01.014
- 64. Kortei, N.K., Wiafe-kwagyan, M., 2014. Evaluating the effect of gamma radiation on
  eight different agro-lignocellulose waste materials for the production of oyster
  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
- 66. Kumar, B., Bhardwaj, N., Agrawal, K., Chaturvedi, V., Verma, P., 2020. Current
  perspective on pretreatment technologies using lignocellulosic biomass: An emerging
  biorefinery concept. Fuel Processing Technology 199.
  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
- 68. Kumari, D., Singh, R., 2018. Pretreatment of lignocellulosic wastes for biofuel
  production: A critical review. Renewable and Sustainable Energy Reviews 90, 877–
  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 microwave978 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
- 70. Lin, R., Cheng, J., Ding, L., Song, W., Liu, M., Zhou, J., Cen, K., 2016. Enhanced
  dark hydrogen fermentation by addition of ferric oxide nanoparticles using
  Enterobacter aerogenes. Bioresource Technology 207, 213–219.
  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
- 76. Mohammadi, P., Ibrahim, S., Annuar, M.S.M., 2012. Comparative study on the effect
  of various pretreatment methods on the enrichment of hydrogen producing bacteria in
  anaerobic granulated sludge from brewery wastewater. Korean Journal of Chemical
  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., Pugalenthi, V., 2014. Comparative
  1011 evaluation of fermentative hydrogen production using Enterobacter cloacae and
  1012 mixed culture: Effect of Pd (II) ion and phytogenic 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
- 80. Muharja, M., Junianti, F., Ranggina, D., Nurtono, T., Widjaja, A., 2018. An integrated
  green process: Subcritical water, enzymatic hydrolysis, and fermentation, for

- biohydrogen production from coconut husk. Bioresource Technology 249, 268–275.
  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 agricultural waste for delignification, rapid hydrolysis, and enhanced biogas 1029 1030 production: A review. Journal of the Indian Chemical Society 98. https://doi.org/10.1016/j.jics.2021.100147 1031
- 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
- 90. Peña, L., Xu, F., Hohn, K.L., Li, J., Wang, D., 2014. Propyl-Sulfonic Acid
  Functionalized Nanoparticles as Catalyst for Pretreatment of Corn Stover. Journal of
  Biomaterials and Nanobiotechnology 05, 8–16.
  https://doi.org/10.4236/jbnb.2014.51002
- 91. Pendyala, B., Rao, S., Lalman, J.A., Shanmugam, S.R., Heath, D.D., Lau, P.C.K.,
  2012. Pretreating mixed anaerobic communities from different sources : Correlating
  the hydrogen yield with hydrogenase activity and microbial diversity. International
  Journal of Hydrogen Energy 37, 12175–12186.
  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
- 93. Penteado, E.D., Lazaro, C.Z., Sakamoto, I.K., Zaiat, M., 2013. Influence of seed
  sludge and pretreatment method on hydrogen production in packed-bed anaerobic
  reactors. International Journal of Hydrogen Energy 38, 6137–6145.
  https://doi.org/10.1016/j.ijhydene.2013.01.067
- 94. Ponnusamy, V.K., Nguyen, D.D., Dharmaraja, J., Shobana, S., Banu, J.R., Saratale,
  R.G., Chang, S.W., Kumar, G., 2019. A review on lignin structure, pretreatments,
  fermentation reactions and biorefinery potential. Bioresource Technology.
  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
- 96. Raj, T., Chandrasekhar, K., Naresh Kumar, A., Kim, S.H., 2022. Lignocellulosic
  biomass as renewable feedstock for biodegradable and recyclable plastics production:
  A sustainable approach. Renewable and Sustainable Energy Reviews 158, 112130.
  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.

- Bioresource Technology 199, 92–102. https://doi.org/10.1016/j.biortech.2015.07.106
  Reddy, K., Nasr, M., Kumari, S., Kumar, S., Gupta, S.K., Enitan, A.M., Bux, F.,
  2017. Biohydrogen production from sugarcane bagasse hydrolysate: effects of pH,
  S/X, Fe2+, and magnetite nanoparticles. Environmental Science and Pollution
  Research 24, 8790–8804. https://doi.org/10.1007/s11356-017-8560-1
- 99. Ren, N.Q., Guo, W.Q., Wang, X.J., Xiang, W.S., Liu, B.F., Wang, X.Z., Ding, J.,
  Chen, Z.B., 2008. Effects of different pretreatment methods on fermentation types and
  dominant bacteria for hydrogen production. International Journal of Hydrogen Energy
  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., Ummalyma, 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
- 105. Shirkavand, E., Baroutian, S., Gapes, D.J., Young, B.R., 2016. Combination 1113 1114 of fungal and physicochemical processes for lignocellulosic biomass pretreatment - A Renewable Sustainable 54, 1115 review. and Energy Reviews 217-234. https://doi.org/10.1016/j.rser.2015.10.003 1116
- 1117 106. Silva, T.L. da, Reis, A., 2016. Algal biorefinery: An integrated approach, in:

- Algal Biorefinery: An Integrated Approach. pp. 1–467. https://doi.org/10.1007/978-3319-22813-6
- 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 Nanobiotechology 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, Castro-Galiano, E., Cardona-Alzate, C.A., 2019. Acid pretreatment of 1138 Е.. 1139 lignocellulosic biomass for energy vectors production: A review focused on operational conditions and techno-economic assessment for bioethanol production. 1140 1141 Renewable and Sustainable Energy Reviews 107, 587-601. https://doi.org/10.1016/j.rser.2019.02.024 1142
- 1143
  113. Suhara, H., Kodama, S., Kamei, I., Maekawa, N., Meguro, S., 2012. Screening
  of selective lignin-degrading basidiomycetes and biological pretreatment for
  enzymatic hydrolysis of bamboo culms. International Biodeterioration and
  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
- 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
  pretreatment methods on anaerobic mixed microflora to enhance biohydrogen
  production utilizing dairy wastewater as substrate. Bioresource Technology 99, 59–
  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., Johir, 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
- 123. Wang, J., Wan, W., 2008. Comparison of different pretreatment methods for
  enriching hydrogen-producing bacteria from digested sludge. International Journal of
  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

- metal ions on the hydrolysis of bamboo biomass in 1-butyl-3-methylimidazolium
  chloride with dilute acid as catalyst. Bioresource Technology 173, 399–405.
  https://doi.org/10.1016/j.biortech.2014.09.125
- 1187 125. Wimonsong, P., Nitisoravut, 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., Nitisoravut, 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
- 129. Yoo, C.G., Pu, Y., Ragauskas, A.J., 2017. Ionic liquids: Promising green
  solvents for lignocellulosic biomass utilization. Current Opinion in Green and
  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 Bioresource 259, 1204 pretreatment. Technology 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
- 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





- 1226 1227
- 1228 Highlights
- Recentlignocellulosic pretreatments have been documented.
- Radiation energy based pretreatment techniques were discussed.
- Role of nanotechnology in bio-H<sub>2</sub> production has been highlighted
- 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: Conceptualization, Writing - original draft, review & editing. Sundaram Arvindnarayan: 1238 Writing – review & editing. Retnam Krishna Priya: Writing – review & editing. Rajesh Banu 1239 J: Writing – review & editing. Young–kwon Park: Writing – review & editing. Vinod Kumar: 1240 Writing - review & editing, Rijuta Saratlae- Writing - review & editing, Gopalakrishnan 1241 Kumar: Writing - review & editing, Funding acquisition, Project administration & 1242 Supervision. 1243

1244

1245 138.

**CERES Research Repository** 

School of Water, Energy and Environment (SWEE)

https://dspace.lib.cranfield.ac.uk/

Staff publications (SWEE)

# 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