

Review

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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>

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

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Abstract

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

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

1. Introduction

The lignocelluloses have been originated from both the edible and non-edible industries and are sustainable as well as promising materials for the productivity of second generation bio-fuels, which mainly include bio-ethanol, bio-H₂, biogas, bio-methane, synthetic bio-fuels, bio-diesel *etc.* Lignocellulosic biomass is a renewable resource and an interesting alternative for 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 biorefinery, cosmetic, food and pharmaceutical industries, as well (Ashokkumar et al., 2022; Kumar et al., 2019; Ponnusamy et al., 2019). In the way, such materials obtained from flowers, energetic willow, grasses, miscanthus, poplar trees, and stems, are functioning as fillers in the fabrication of beauty masks, curative chows and thermoplastic composite materials. Some other significant sources of the lignocellulosic biomass materials are the residual forms procured from 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 of plants as well as firewood (Azbar et al., 2009). The biomass structure only defines the kind of pretreatment techniques, required. The bio-H₂ that is procured from lignocelluloses *via* fermentation is an alternative to petro-derived fuel itself as it is eco-friendly since there is no emission of GHGs (greenhouse gases), mainly CO₂ (carbon dioxide) while its combustion (Moreno and Dufour, 2013). Further, bio-H₂ is a basic molecule in a range of chemicals as well as petro-chemical processes, like production of ammonia, integrated circuits and optical fibers, methanol, methane, nitrobenzene derived aniline from nitrobenzene, polymers syn-gas, hydrogenation derived olefins, *etc.* Bio-H₂ is also used in the petro-chemical processes of hydro-amination, hydro-cracking and hydro-conversion (Gómez et al., 2011). Beyond from the lignocellulosic bio-energy source, the bio-H₂ can crucially be generated with energetic 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. All such processes not only need a high input of electrical power and fossil fuels utilization but also depletion of green environment by means of air pollution. So, bio-resources have been considered for larger scale production of bio-H₂ (Goryunov et al., 2016). In such a way the biomasses can be an alternative option to produce sustainable bio-H₂ energy to achieve short-

term emission reductions (Balat, 2011). In the Europe, about 67% of preliminary energy has been procured primarily from biomass renewable resources with nearly about 14–19 MJ/kg 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 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 circumstances (Sun and Cheng, 2002). The main by–products of bio–refineries apart from the bio–H₂ are the biomaterials and certain bio–chemicals *viz.* bio–ethanol and furan are very important for environmental energy security as it possesses socio–economic advantages associated with biodiversity, food security, reduction of greenhouse gases emission, and sustainable bio–energy development (Balat, 2011; Sun and Cheng, 2002). The generation of energy/power forecasts that the produced energy has been raised from 200 TWh by the year of 2006 to 380 TWh by the year of 2016, globally and it has reached 600 TWh in 2020 (IEA, 2015). The limitation of lignocellulosic derived bio–H₂ *via* fermentation is the formation sugar intermediates during hydrolysis. Thereby, it requires a proper lignocellulosic pretreatment in bio–H₂ productivity. The aim of the pretreatment technique includes change in the rigid lignocellulosic by means of digestion to increase the accessibility of a range of hydrolytic reagents/factors like suitable chemicals, enzymes, *etc.*, for the decomposition of organic matters. These can be metabolized by fermentation process with the support of microorganisms. The lignocellulosic biomass derived bio–H₂ production necessitates the development in commercially and eco–friendly technologies towards the pretreatment process (Hendriks and Zeeman, 2009). In this concern, the lignocellulosic biomass pretreatment techniques on its structure have highlighted herein with the pros and cons of each technique, especially about the cellulose digestibility. This review mainly focuses on novel and advances physical, chemical, physico–chemical, microbiological and nanotechnology based pretreatment techniques towards lignocellulosic biomass pretreatment for bio–H₂ production *via* fermentation.

2. Lignocelluloses and pretreatments

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

are all the key facts to make the cell resistant/accessible to chemical and bio reagents. Thereby, the recalcitrance of lignocellulosic biomass materials has been done eventually by means of the pretreatment techniques as they hold a prominent role in the utilization of those biomass materials towards industrial applications. Before the downstream process of disintegration of complex lignin structure, using the suitable pretreatment techniques can be employed for reducing the crystallinity and solubilization of hemicellulose content. Thereby, the accessibility of reagents/enzymes and enhancement of their activity over the surface has been increased towards the lignocellulosic biomass materials (Abraham et al., 2020). The suitable pretreatment 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 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 polysaccharides of the lignocellulosic materials into simple monomers and are easily metabolizable / easily producing fermentable sugars to yield bio-H₂. There is further conversion of valuable bio-H₂ while the hydrolytic process with low energy consumption, accompanied by the formation of non-toxic enzyme inhibitors, *etc* (Abraham et al., 2020; Dharmaraja et al., 2019; Mankar et al., 2021; Usmani et al., 2020). Recently, various pretreatment techniques have been employed for dissimilar lignocellulosic materials and each technique possesses its own pros and cons. There are five kinds of pretreatment techniques (Fig. 1) viz. (i) physical, (ii) chemical, (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; Kucharska et al., 2018; Singh et al., 2018), which all are widely been employed for the lignocellulosic materials pretreatment processes. Each technique follows its own characteristic experimental conditions to break the complex structure of lignocellulose materials to yield bio-H₂ and a range of value added products, besides.

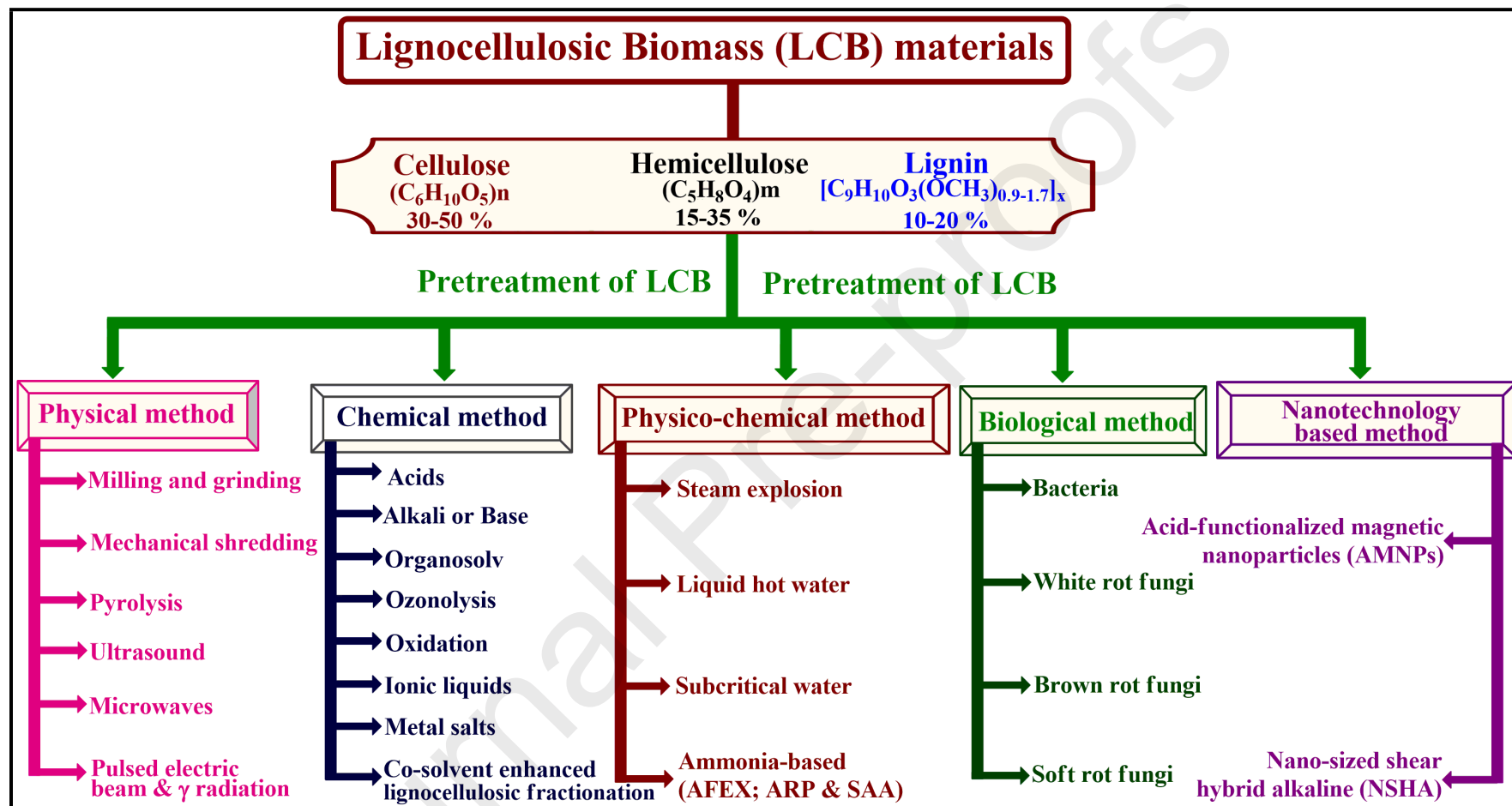


Fig. 1. Various pretreatment methods for lignocellulosic biomass materials.

3.1. Lignocellulosic pretreatment by physical methods

The pretreatment by physical processes strongly enhances the hydrolytic efficacy and the decomposition of biomass anaerobically not only to liquid as well as gaseous bio-fuels but also some other value added bio-products (Chandel et al., 2022; Sinha and Pandey, 2011). Abbasi and Abbasi (Abbasi and Abbasi, 2010), has shown the bio-H₂ productivity by means of fermentation possibly increases during mechanical/physical pretreatment. Further, it 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 mainly include mechanical shredding (grinding *via* chipping, milling); steam explosion & AFEX (Ammonia fiber/freeze expansion), pyrolysis, radiation energy-based microwaves, pulsed electric field and ultrasound techniques.

3.1.1. Mechanical shredding and Pyrolysis

Mechanical shredding (grinding *via* chipping, milling) for soft biomass at a temperature of about 50–70 °C) leads to rupture the lignocellulosic fibers and thereby reduces the period of time duration to digest the materials upto about 23–59% for further treatment to yield fermentative bio-H₂ (Guo et al., 2012; Singh et al., 2022). The fractionation of the shredded materials by means of sieves system makes the particles finer then it consequently 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 simultaneously the downstream conversion and processing of the lignocellulosic components (Martin-Sampedro et al., 2012). Though such an overall mechanical pretreatment process is 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 materials but not to produce bio-H₂, instead a mixture of syn-gas and bio-oil (Karimi and 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.

3.1.3. Irradiation processes

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

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 application of microwave radiation for 5 min on sugarcane bagasse with water (distilled), acid of phosphorus (H_3PO_3 ; pH=3.0) and glycerol of about 10 % indicates that 5.4 % (w/w) 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 by means of the enzymatic hydrolysis of hemicelluloses (22.4 %) and celluloses (40.2 %) (Singh et al., 2022). The pulsed electric field in the form of γ radiation possesses highly penetrating power (Kortei and Wiafe-kwagyan, 2014; Singh et al., 2022). Thereby, it can be applied to thick materials, and it results in the biomass degradation to overcome biomass recalcitrance, followed by solubility increase and decrease in mechanical strength. Conversely, this technique has not been applied in industrial scale, owing to its costs and environmental as well as some safety issues. Among the non-thermal technologies pulsed 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 understood. However, to achieve many of these processes require very high treatment intensities, and duration from microseconds to milliseconds may cause temporary effects only (Kortei and Wiafe-kwagyan, 2014; Singh et al., 2022). Moreover, inactivating pulsed electric field is the safety measure as per the International guidelines and national safety standards for electromagnetic fields, which are developed on the basis of the current scientific knowledge. I- γ radiation has high potential, though its development and commercialization has been obstructed in the favor of public perceptions. Furthermore, the employment of ultrasonication 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 *via* breaking of inter molecular hydrogen linkages (Kucharska et al., 2018) for producing fermentative bio- H_2 , more effectively. Conversely, the economic viability on the fermentation to yield bio- H_2 obviously can be led by mechanical pretreatment, correlated to high energy operations for the mechanical biomass chipping fragmentation (Kucharska et al., 2018).

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-H₂. The common chemicals such as H₂SO₄, HCl, HNO₃, H₃PO₄, HCOOH, CH₃COOH, NaOH, KOH, Ca(OH)₂, NH_{3(aqu)}, H₂O₂, *etc.*, are widely utilized in this pretreatment process.

3.2.1. Acid pretreatment

In acid pretreatment method, when the lignocellulosic biomass materials are pretreated with inorganic and organic acids such as HCl, H₂SO₄, HNO₃, H₃PO₄, formic acid, oxalic acid, maleic acid, *etc.*, generate the hydrogen (H⁺) ions, which breakdown the glucosidic chain bonds present between long cellulose and hemicellulose chain into simple 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 (30–70 % at < 100 °C) or dilute acids (0.2 – 2.5 w/w % or 0.5 – 10 % v/v at 120 – 250 °C) to the LCB materials (Badiei et al., 2014). Dilute H₂SO₄ pretreatment is commonly used for poplar, switch grass, spruce, and corn stover feedstocks. The conc. acid pretreatment can accelerate a high sugar conversion rate (> 90 %) and these acids are more toxic as well as corrosive in nature. Also, the utilization of conc. acids causes the undesired cellulose 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 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 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 (Baruah et al., 2018; Ravindran and Jaiswal, 2016; Sahoo et al., 2018; Zheng et al., 2014). Sahoo et al., (Sahoo et al., 2018) reported the effect of dilute H₂SO₄ (0.4 %) and NaOH (1 %) pretreatment on wild rice grass (*Zizania latifolia*) for enzymatic hydrolysis and showed 163 and 92 mg sugar g⁻¹ respectively. This study proves the dilute mineral acids pretreatment process is more effective than alkali methods. Furthermore, the organic acids such as oxalic, maleic, citric and formic acids are more efficient than dilute mineral acids for LCB pretreatment for efficient industrial scale fermentative production of bio-H₂ (Baruah et al., 2018).

3.2.2. Alkaline pretreatment

Alkaline or base pretreatment involves the addition of alkaline reagents or bases (such as NaOH, KOH, $\text{Ca}(\text{OH})_2$, NH_4OH , *etc*) to lignocellulosic biomass materials leading to an increase of internal surface by swelling, decrease of cellulose crystallinity & polymerization, destruction of chemical links between lignin and other polymer units i.e., cleavage of ester and other linkages between lignin and hemicellulose or other carbohydrate moieties, lignin breakdown, solvation of hemicellulose *etc* (Amin et al., 2017; Ashokkumar et al., 2022; Kim et al., 2016; Nahak et al., 2022), as a result a high conversion hydrolysis rate of cellulose into fermentable sugar units either by enzymatic or microorganisms hydrolysis. Generally, the alkaline pretreatment is more effective for hardwood, agricultural residues, herbaceous crops, *etc* with low content of lignin. However, the excessive use of NaOH may cause inhibition of 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., 2018), investigated the NaOH and Na_2CO_3 pretreatments on wheat straw at 0 °C for 6 h and showed a solid dissolution efficiency of 86.7 and 91.1 %, respectively. They also showed an 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 NaOH pretreatment on vinegar residue (VR) showed an increased CH_4 yield (205.86 mL g^{-1} at 3% NaOH), that is 54 % higher than the untreated VR. Zhu et al., (Zhu et al., 2010) 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 [$\text{Ca}(\text{OH})_2$] 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 ones. The major benefit of alkaline pretreatment is efficient for removal of hemicellulose and lignin, to increase the surface area for further hydrolysis process, but this pretreatment causes 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., 2016; Vu et al., 2020). Effects of acidic and alkaline pretreatments on bio- H_2 production are given in Table 1.

289 Table 1. Effects of acid and alkali on bio-H₂ production through inoculum pretreatment [Adopted from modified Ref. (Bundhoo et al.,
290 2015)].
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Inoculum pretreatment	Pretreatment Conditions	Yield of bio-H ₂	References
Anaerobic inoculum	Substrate: Glucose Acid: 2.0 M HCl pH: 3.0 (24 h)	Control: 1.54 meq mol ⁻¹ glucose Treated: 3.00 meq mol ⁻¹ glucose Yield : + 94.80 %	(Chaganti et al., 2012)
	Substrate: Glucose Alkali: 3.0 M NaOH pH: 11.0 (24 h)	Control: 1.54 meq mol ⁻¹ glucose Treated: 2.80 meq mol ⁻¹ glucose Yield : + 81.80 %	
Activated sludge	Substrate: Glucose Acid: 1 M HCl pH: 3.0 (24 h)	Control: 0.38 mol mol ⁻¹ glucose Treated: 1.51 mol mol ⁻¹ glucose Yield : + 297.40 %	(S. Chang et al., 2011)
	Substrate: Glucose Alkali: 1 M NaOH pH: 10.0 (24 h)	Control: 0.38 mol mol ⁻¹ glucose Treated: 1.34 mol mol ⁻¹ glucose Yield : + 252.60 %	
Anaerobic inocula	Substrate: Glucose Acid: HClO ₄ pH: 2.0 (10 min)	<i>Without pre-acidification</i> Control: 60.5 ml Treated: 311.0 ml Yield : + 414.0 %	(Cheong and Hansen, 2006)

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

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

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

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

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

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

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3.2.3. *Organosolv pretreatment*

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

3.2.4. *Ozonolysis pretreatment*

In this pretreatment method, the powerful oxidant say ozone (O_3) 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

oxidized into soluble low molecular weight carboxylic acid compounds such as AcOH, HCOOH, *etc.* The efficiency of enzymatic hydrolysis treatment of LCB by O₃ has enhanced upto 5–folds and also forms no toxic hydrolysis end–products. Silverstein et al., (Silverstein et al., 2007) studied the ozone pretreatment of cotton stalk (10 5 w/v; Temp. 4 °C; Time 30–90 min) showed the reduced lignin content of 11.97–16.60 % and the solubilization of xylan (1.9–16.7 %) and glucan (7.2–16.6 %), which is comparatively lower by this treatment than alkali NaOH process. The great merit for this pretreatment method is no generation of 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 enzymatic hydrolysis yields of wheat and rye straw upto 89% and 57% respectively, while for the untreated wheat and rye straw the enzymatic hydrolysis yields were 29 % and 16 % respectively.

3.2.5. *Oxidation pretreatment*

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

3.2.6. *Ionic liquids (ILs) pretreatment*

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

and anions (such as acetate, chloride, bromide, sulphate, methanoate, nitrate, sulphate, triflate, *etc*) in the liquid state with lower melting point ($< 100\text{ }^{\circ}\text{C}$) and low vapour pressure, as well (Baruah et al., 2018; Behera et al., 2014; Bensah and Mensah, 2013; Brandt et al., 2013; Yoo et al., 2017). ILs is also act as green solvents (GSs) because they possess low vapour pressure, melting point, non-volatility, non-toxicity, high thermal and chemical stability, *etc* (Yoo et al., 2017). During the ILs pretreatment process, both anions and cations form a strong inter- and intramolecular hydrogen bonding with cellulose and other 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 cations, hence, the cellulose moiety can undergo precipitation and the lignin can be dissolved in ILs (Chen et al., 2017; Yoo et al., 2017). Some of the ILs like 1-ethyl-3-methylimidazolium diethyl phosphate-acetate, 1-butyl-3-methylimidazoliumacetate, 1-butyl-3-methylimidazoliumchloride, 1-butyl-3-methylimidazoliumacetate, 1-benzyl- 3-methylimidazoliumchloride, 1-butyl-3-methylimidazoliummethylsulfate, 1-ethyl-3-methylimidazoliumgroups, 1,3- dimethylimidazolium groups, cholinium amino acids, 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, 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 Amimcl (1-allyl-3-methylimidazolium chloride) and Bmimcl (1-butyl-3-methylimidazolium chloride), which may be effectively applied for cellulose dissolution when the temperature is $< 100\text{ }^{\circ}\text{C}$ (Baruah 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 glucose yield, when the temperature was increased from 125 to 150 $^{\circ}\text{C}$ at 2 h. Das et al., (Das et al., 2021) reported the enzymatic hydrolysis and ethanol fermentation of several wood materials with two different ionic liquids namely cholinium lysinate [Ch][Lys] and ethanolamine acetate [EOA] [OAc] generated 24–84 % of glucose and 14–80 % of xylose. Rahim et al., (Rahim et al., 2020) investigated the combination of ultrasound irradiation and three different ILs [Emim][OAc], [Emim] [Cl], [Emim][HSO₄] pretreatment of bamboo provided 63.99 % of cellulose and 14.99 % of lignin.

3.2.7. *Metal salts pretreatment*

The metal salts pretreatment of LCB materials requires a high pressure reactor i.e., the biomass materials are loaded in the reactor along with the metal chlorides such as ZnCl_2 , FeCl_3 , FeCl_2 , CrCl_2 , MnCl_2 , AlCl_3 , *etc* and then heated to 170–180 °C for 20–30 min (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 pretreatment of bagasse with metal chlorides in dilute acidic medium followed by enzymatic 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 the effluent. Wang et al., (Wang et al., 2014) investigated the hydrolysis of bamboo biomass by dil. HCl in the presence of 1-butyl-3-methylimidazolium chloride with Cu^{2+} ion showed a maximum sugar yield of 67.1 % at 100 °C.

3.2.8. *Co-solvent enhanced lignocellulosic fractionation (CELf)*

In this CELF method, a mixture of tetrahydrofuran (THF) and H_2O 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_2SO_4 (act as catalyst) on enzymatic hydrolysis of switchgrass biomass, yielded approximately 90 % glucose at 160 °C.

3.3. *Physico-chemical pretreatment*

Among physico-chemical pretreatments such as steam explosion (SE), liquid hot water (LHW), subcritical water (SCW) and ammonia-based methods are promising to breakdown the recalcitrant structure of LCB materials. The liquid hot water and steam explosion processes release very high concentrations of degradation compounds *viz.* furfural, 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, 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 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)

can easily disintegrate the cellular components by means of lignocellulosic biomass digestion 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. Similar way, the AFEX technique has been considered as efficient process with low content 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 113.5 million liters butanol per year. Barbanera et al., (Barbanera et al., 2015) investigated 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 MPa; Time: 15 min). Vivekanand et al., (Vivekanand et al., 2014) reported the combined sequential SO₂ with steam explosion methods, followed by enzymatic hydrolysis that showed more effective polysaccharide conversion upto of 81 %. The LHW pretreatment is an ideal method for the lignocellulose substrates where the addition of chemicals for delignification can result in effective utilization of the biomass. The process is performed only in the customized high pressure reactor. This method is similar to the steam explosion method and 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 al. (Muharja et al., 2018) studied the combined green process of subcritical water (SCW) and enzymatic hydrolysis for bio-H₂ fermentation from coconut husk and the maximum bio-H₂ yield, up to 0.279 mol/mol by consumption of sugar, which is lower than the other works. Further, ammonia (NH₃) is an effective agent for the pretreatment of LCB materials. There 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 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., 2022; Ravindran and Jaiswal, 2016). Also, the AFEX pretreatment is most appropriate 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.*, showed > 90 % of glucose yield, during simultaneous saccharification and fermentation process. After the completion of pretreatment, the vaporized NH₃ has been collected, recycled and reused again. Jin et al (Jin et al., 2016) reported that the Great Lakes Bioenergy Laboratories in the US have demonstrated the AFEX pretreatment method for cellulosic ethanol production, which reduced enzyme loading by 66 % and also increased EtOH

productivity by 129 %. In an ARP pretreatment process, the poplar wood is soaked in 15 % of NH_3 (aqu.) 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.

3.4. *Biological pretreatment*

Biological pretreatment process is more superior to the other methods (Anu et al., 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 rate. During the biological pretreatment of LCB materials, the microorganisms such as bacteria, fungi, enzymes, metabolites from enzymes, *etc* are playing a vital role before the enzymatic hydrolysis of LCB components (Dey et al., 2022; Hassan et al., 2018). The key 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 materials to produce fermentative bio- H_2 (Dey et al., 2022; Hassan et al., 2018). Certain microorganisms are present in nature, which exhibit cellulolytic and hemicellulolytic 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 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 wood polysaccharides however; the alteration of lignin is limited extent only. The commonly utilized white rot fungi like *Cyathus stercoreus*, *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Ceriporiopsis subvermispora*, *Ceriporia lacerata*, *Pycnoporus cinnabarinus*, *Cyathus stercolerus*, *Cyathus cinnabarinus*, *Ceriporia lacerata*, *Ceriporiopsis subvermispora*, *Pycnoporus cinnabarinus*, *Pleurotus ostreatus*, *Trametes pubescens*, *etc.*, are frequently applied to degrade lignin because these species contain lignin degradation enzymes, including peroxidase and laccase (Anu et al., 2020; Hassan et al., 2018). In addition to some *Basidiomycetes* species, such as *Bjerkandera adusta*, *Irpex lacteus*, *Fomes 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, such as lignin peroxidase, manganese peroxidase and versatile peroxidase, are generated from various microorganisms, which also degrading the lignin structure completely by increasing

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

3.5. Nanotechnical pretreatment

Nanotechnology-based pretreatment on lignocellulosic biomass structures is an important methodology to yield bio-H₂. Since the reagents can be easily recycled and reutilized, so it reduces the cost of the process (Chandel et al., 2022). The type of acid-functionalized magnetic nanoparticles (AMNPs) is applicable to the pretreatment of LCB. The AMNPs utilization to enzymatic immobilization, functionalization by means of microbes/chemicals is an alternative to the traditional pretreatment techniques for lignocellulosic biomass. Reusable nature of AMNPs and enzymes obviously is the cost-effective and eco-friendly systems. Nano-sized shear hybrid alkaline (NSHA) catalysts also often utilized for pretreatment techniques for lignocellulosic biomass. The nano-sized metal 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).

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).

3.5.2. NSHA pretreatment

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

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 certain additives namely PDAC [Poly(diallyldimethylammonium chloride)] and are utilized in the degradation of lignocellulosic biomass constituents. Such kind of produced charged components function as polyelectrolytes to modify surface of the cellulose and thereby stabilization of the lignin occurs. It has been shown that there is generation of globular complexes with lignin components by means of PDAC, and it can alter the biomass cell wall morphology. Further, the PDAC polyelectrolyte reduces utilization of chemical reagents necessitated by the pretreatment of lignocellulosic biomass constituents (Dey et al., 2022).

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

Production of bio-H₂, using nano-materials in the bio-fuel industry is very attractive 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-materials can act as cofactors (like hydrogenase), consequently reduces the exchange of H⁽⁺⁾(protons) (Dey et al., 2022). The function of the microbes has been greatly influenced by increasing the metal NPs concentration to yield bio-H₂. Such a nano-approach improves the rate of e⁽⁻⁾ (electron) transfer that suitably improves the metabolic activity of the micro-biota. It has also been demonstrated that the metal NPs can improve the production of bio-H₂ in acidic pH, moreover the substrate concentration increases with decrease of bio-H₂ production, *i.e.*, inverse effect. It was found that the metal oxide NPs can increase 4.5 times of the bio-H₂ production, as compared to normal synthetic processes. Similar way with iron NPs (0.2 g/L), nearly a 33% increase in the bio-H₂ production was observed in sugar (sucrose) medium (Han et al., 2016). Further, 260% conversion of sugar composition by means with a combination of lignocellulosic substrates and Ti(titanium) NPs. Though, the impact on dark fermentation of bio-H₂ production by means of nano-material is still not 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 lignocellulosic components only converted effectively to bio-H₂ and the residues produce some other by-products. Thereby, there a necessity is to upgrade the technique for industrial production of bio-H₂ by lignocellulosic substrates *via* improvement/introduction of suitable strain as well as nano-materials.

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

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

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

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

581

582 4. Research needs Perspectives and Future Directions

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

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

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 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 challenges fall in the category of intensively energy requirement, low process efficiency, generation of toxic or environmentally hazardous wastes/inhibitors, perturbation in the overall yield on fermentable sugar moieties, degradation of partial cellulose and lignocellulosic structure, *etc.* (Chauhan, 2020). Now, there is an emerging need for an 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 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 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

the usage of water as well as energy sources and (iii) operation of integrated process to use 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), which are easily miscible in water and the recovery of catalysts from waste water streams are more energy intensive and expensive process *i.e.*, using phosphoric acid pretreatment process results in the formation of very high digestible amorphous cellulose content, but the recovery of acid from aqueous medium is more difficult and expensive process. Further, in some pretreatment processes, the neutralization of chemicals by the additions of acid or base, generate some salts or compounds which cause an additional cost for recovering and recycling with water from consequent processing steps because another major challenges (Janusz et al., 2020, 2017). The LCB pretreatment processes include mechanical processing, microwave irradiation processing, wet oxidation, ozonolysis, hot water and supercritical CO₂ and H₂O 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 expensive reactor units (Balan, 2014). Till now, the challenge for the effective enzymatic 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 pretreatment technology must be upgraded with effective reactor systems with capable of performance at high solid concentrations with large particles and different variety of LCB 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 than the other technologies (Ponnusamy et al., 2019; Testa and Tummino, 2021).

Pretreatment steps for lignocellulosic biomass materials to fermentable sugars are a challenge in the case of large-scale conversion for procuring cost-effective and competitive technically derived products along with very low inhibitory concentration. Agricultural residues have been utilized for industrial bio-fuel production *via* steam explosion, as it is an important technology. This steam explosion in a 50 m³ industrial reactor with corn-stover was performed, to yield 80% of hemicelluloses and then by hydrolysis more than 90 % of celluloses were recovered (Kucharska et al., 2018). Pretreatment with dil. acids is 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 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,

pressure, time of retention, solid:liquid ratio and temperature. Silva et al., (Silva and Reis, 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 pretreatment process using LHW turned as a commercial one. The novel approach to lessen the technical issues with the performed pretreatment processes in a single operation, is concerned to combination of those processes *via* mechanical (crushing)–chemical, –electron beam– chemical (alkali), –microwave–chemical, –chemical–steam explosion and physical–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 well, in turn the combination of such processes can considerably progress the effectiveness of enzyme hydrolysis. Binod et al., (Binod et al., 2012) employed a combination of microwave–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 short period of time duration. Lai et al., (Lai and Idris, 2016) has suggested low–energy ultrasound–chemical (–alkali) pretreatment for the enhancement of biodegradable nature of 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 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 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 lignocellulosic biomass biofuels by fermentation, the wastewater management has given to importance as the biorefinery stillage contains a range of dissolved and unutilized fermentable sugars mainly lignin of about 74.1–79.0 wt. % of the total biomass (Trinh et al., 2013). Consequently, this lignin has been utilized for the production of high–value added products/by direct combustion to supply sufficient energy for the industrial processes. In this 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 bio-oil, bio-char, *etc.* (Trinh et al., 2013). But for the production of gaseous bio-fuels 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 heat/energy generating integrated process. Thereby, integrated technologies for the production of bio-H₂ are taken into consideration because utilization of value added products

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-H₂, high cost and low yields along with comparatively low concentration of fermentation broth are still some major challenges.

The chemical pretreatment conventionally is utilizing acids and bases and it can be regarded as a cost-effective process. The by-products formed in this process should be purified and reused in the form of value-added products. Such kind of technique is commercially viable to treat the lignocellulosic biomass feed for bioconversion processes, while bio-fuels and other value added bio-products are derived. The recent familiar pretreatment techniques are generally energy-intensive. Thereby, the development on resourceful and cost-effective pretreatment processes is given significance in an industrial point of view. There, a popular industrial chemical pretreatment technique offers highly digestible biomass feed. Then, the recycling, recovery and utilization of liquids and solids 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 technologies for improving production of bio-H₂ from the DF process can be categorized according to their pretreated inoculums/substrates. They can be classified into physical, chemical, physico-chemical, biological and nano-technical pretreatments, based on the biomass used. Amongst, the dissimilar technologies reviewed, acid pretreatments are the mostly studied techniques for the substrates and inoculums. The most suitable emerging techniques over different studies, the hybrid/combined technologies have been given maximum yield. In addition, many pre-techniques have been employed for substrates pretreatment that may eventually form inhibitory compounds thereby can decrease bio-H₂ 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 energy consumption and technical feasibility in economic aspect. In the case of substrates, 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 concluded that among the various pretreatments investigated for such kind of wastes, ultrasound, combined and biological pretreatments have been utilized/employed to procure positive results.

5. Conclusions

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

Acknowledgement:

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

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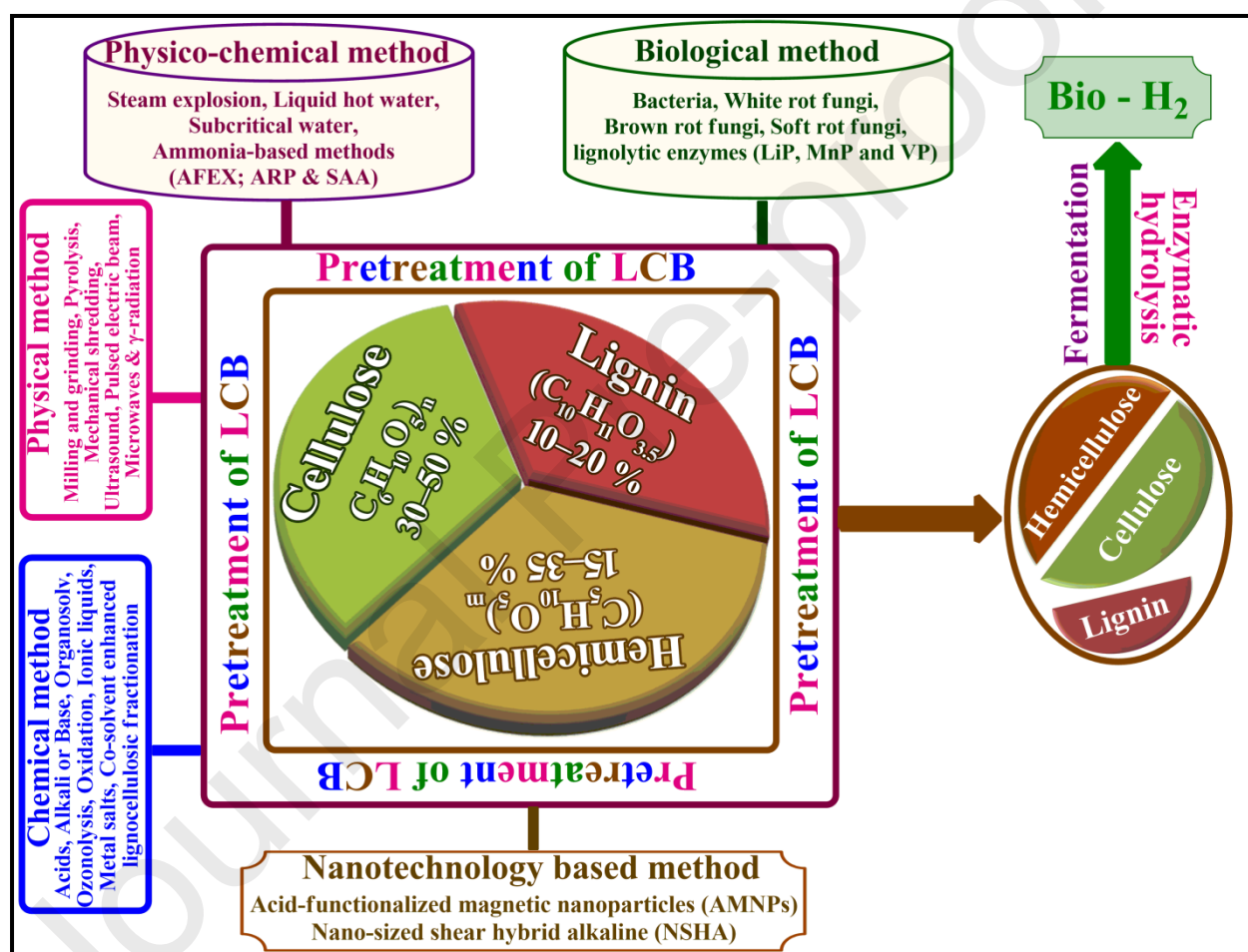
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Graphical Abstract



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Highlights

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

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CRedit authorship contribution statement

Chyi-How Lay: Conceptualization, Writing – original draft & editing. Jeyaprakash
Dharmaraja Conceptualization, Writing – original draft, review & editing. Sutha Shobana:
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J: Writing – review & editing. Young-kwon Park: Writing – review & editing. Vinod Kumar:
Writing – review & editing, Rijuta Saratlae– Writing – review & editing, Gopalakrishnan
Kumar: Writing – review & editing, Funding acquisition, Project administration &
Supervision.

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

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2022-10-12

Elsevier

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

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