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Lignocellulosic biomass conversion *via* greener pretreatment methods towards biorefinery applications

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2 **biorefinery applications**

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Lignocellulose biomass during pretreament release various copmounds, among them important one is reducing sugars, which can be utilized for the production of biofuels and some other products. Thereby, innovative greener pretreatment techniques for lignocellulosic materials have been considered to open a new door in the aspects of digestibility of the rigid carbohydrate–lignin matrix to reduce the particle size and remove hemicellulose/lignin contents to successfully yield valid bioproducts. This article reviews about the composition of lignocelluloses and emphasizes various green pretreatments viz novel green solvent–based IL and DES, steam expolsion, supercritical carbon dioxide explosion (Sc–CO2) and co–solvent enhanced lignocellulosic fractionation (CELF) along with suitable mechanistic pathway of LCB pretreatment process. Finally, this article concludes that the existing pretreatments should be redesigned to conquer the demands by large scale production and suggests combined pretreatment methods to carry out various biomass pre–processing.

Keywords: *Lignocellulose; Pretreatments; ILs; DES; Sc–CO$_2$; CELF.*

1. Introduction

Recently, there is a rapid depleteion in petrochemical or fossil fuel products that leads to drastic variation of the universal economic, environmental and pulic health issues. Hence the researchers are looking for and focussing their investigations towards the alternatives for fossil fuels as well as low cost–carbon rich bioenergy sources *via* the utilization of high carbon lignocellulosic biomass (LCB) materials (Anu et al., 2020; Dey et al., 2022; Loow et al., 2018; Mankar et al., 2021; Rasool et al., 2021; Thanigaivel et al., 2022). Due to vast accessibility and quantity of LCB materials from present agricultural region *via* fruits as well as vegetables, forestry wastes, *etc* (Bundhoo and Mohee, 2018; Hassan et al., 2018; Usmani et al., 2020) have been considered as alternative substrates for fossil fuels and also generation of high value added biofuels, chemicals and other by–products (Anu et al., 2020; M. U. Khan et al., 2022). The plant biomass *i.e.*, lignocellulosic biomass material is the most abundant renewable carbon resource and is mainly composed of celluloses, hemicelluloses and lignins. Mostly, the agricultural and food processing industries produce lignocellulosic wastes upto about 1.3 billion tons/year. The valorization of waste plant biomasses *i.e.*, waste lignocellulosic biomass materials obviously create an innovative idea towards commercial gain in rigorous waste disposal and environmental protection point of view. Though, structural conformation, high content of lignin and crystalline nature of celluloses hold back their effective utilization for value addition. The preference of pretreatment selection is entirely based on the physical and chemical nature of biomass materials to release maximum of reducing sugars *via* the pretreatments.

Generally, the LC (lignocellulose) biomass is consisting of 30–50 % of cellulose $[(C_6H_{10}O_5)_n]$, 15–35% of hemicellulose $[(C_5H_{10}O_5)_m]$, and 10–20 % of lignin $[(C_{10}H_{11}O_{3.5})]$ (Ashokkumar et al., 2022; Behera et al., 2014; Henning Jørgensen et al., 2007; Mankar et al., 2021) and also the maximum % of cellulosic moiety is existing in different kind of LCB materials. In most of the plant cell wall, the LCB materials contain both cellulose and hemicellulose moieties, which are very intently associated to lignin content. Consequently, the pretreatment method is essentially required to generate a simple sugar or carbohydrate contents by enzymatic hydrolysis as well as fermentation process *i.e.*, to change the structure of LCB to make the availability of celluloses by enzymatic hydrolysis process, and convert the complex

93 carbohydrate polymeric units into simple fermentable sugar units *via* fermentation process
94 (Amin et al., 2017; Ashokkumar et al., 2022; Binod et al., 2012; Mankar et al., 2021). During the
95 various pretreatment methods, the main objectives are to increase the efficiency of LCB
96 hydrolysis by the enhancement in the enzyme accessibility, partial removal of the lignin as well
97 as hemicellulose contents, increase in the porosity of the LCB materials and decrease in the
98 cellulose crystallinity nature (Amnuaycheewa et al., 2016; Behera et al., 2014; Mankar et al.,
99 2021; Rasool et al., 2021; Thanigaivel et al., 2022). Generally, four efficient LCB preteramnet
100 methods such as physical, chemical, physico–chemcial and biological processes have widely
101 been utilized to convert the LCB materials into bio–fuels and value added bio–compounds
102 (Ashokkumar et al., 2022; Chen and Wan, 2018; Dahunsi, 2019; Li et al., 2021; Lorenci
103 Woiciechowski et al., 2020; Mankar et al., 2021; Muharja et al., 2018; Rebello et al., 2020).
104 During the saccharification process, the pretreated LCB materials are hydrolysed *via* certain
105 cellulolytic and xylanolytic enzyems that convert hemicelluloses and celluloses into simple
106 monomeric sugar units, which are further fermented into desired high value added biofuels and
107 biocompounds *via* certain microorganisms (Anu et al., 2020; Mankar et al., 2021).

108

109   The effective and economically feasible LCB pretreatment methods mainly depend on (i)
110 less energy–intensivity, (ii) cost–effectivity, (iii) reduction in the cellulose crystallinity, (iv)
111 decrease in the LCB particle size, (v) excellent surface area of enhanced enzymatic hydrolytic
112 process, (vi) utilization of low cost and eco–friendly chemicals or solvents, (vii) formation of no
113 enzyme/toxic compounds or corrosive inhibitors, and (viii) delignification of the LCB materials
114 without modification of native lignin structure (Anu et al., 2020; Ashokkumar et al., 2022;
115 Mankar et al., 2021; Rasool et al., 2021). The physical pretreatment processes that include
116 concentrated or mild inorganic mineral acids (H_2SO_4, HCl, HNO_3, etc) and organic acids (say
117 acetic acid, oxalic acid, fumaric acid, maleic acid, etc) are effectively transfigure and detachment
118 of the LCB materials into simple C5 (pentoses) and C6 (hexoses) units. Some of the key factors
119 like crystallinity of celluloses, biomass porosity, active surface areas, rate of hydrolysis, degree
120 of acetylation & polymerization, etc., are delineating the pretreatment processes industrial and
121 energy oriented as well as making eco–friendly feasibility (Anu et al., 2020; Ashokkumar et al.,
122 2022; Rasool et al., 2021). Hence, this present review provides a detailed information on the
123 recently developed greener approaches *viz* ionic liquids (ILs), deep eutectic solvents (DESs),

124 steam explosion (SE) or steram pretreatment (SP), Supercritical carbon dioxide (Sc–CO_2) and

125 co–solvent enhanced lignocellulosic fractionation (CELF) pretreatments. A widespread

126 description on development of the accessible pretreatment methods are also covered and this

127 review will help the readers getting an unambiguous details on the recent advances in the greener

128 pretreatment methods and also inspire them working on novel pathways for upgrading of a LCB–

129 based refinery in the near future.

130

131 **2.   Lignocellulosic materials**

132

133   Based on the resource of LCB materials, the specific structural compositions of

134 lignocellulosic content could be varied. Table 1 summarizes the various LCB material sources

135 with their structural compositions. Most of the LCB materials are comprised of polysaccharides,

136 which are altered into simple monosaccharides or sugar units *via* numerous fermentation

137 processes (Bajpai, 2016a). In general, the fermentable sugar compositions of celluloses,

138 hemicelluloses and lignins are mainly depending on the nature of LCB biomass materials. The

139 rigid cell wall strucrure of the plants is comprised of cellulose, which is overcovered by lignin

140 and hemicellulose moieties. Table 1 clearly has shown that the high percentage of cellulose and

141 hemicellulose contents are predominantly present in LCB materials. The ~ 30–50 % of celluloses

142 [$(C_6H_{10}O_5)_n$] are the primary as well as significant key chemical components of LCB materials.

143 The primary cell wall of cellulose structure is mainly comprised of very stable linear amphiphilic

144 homopolysaccharide polymers of β–D–glucopyranose moieties in the range of 10,000–15,000

145 D–glucose or cellobiose (monomeric) units, which are linked *via* (β–1–4)–glycosidic bonds to

146 form more microcrystallinity (50–90 %) with less amorphous (10–45 %) structural nature (Agbor

147 et al., 2011; Bajpai, 2016a; Bhatia et al., 2020; Lorenci Woiciechowski et al., 2020; Mankar et

148 al., 2021). The linear long chain amphiphilic homopolysaccharide polymers of celluloses are

149 staked as multiple overlapping layers to the axial position of –OH groups. The air stable

150 polymeric long cellulose chains of cell wall structure are formed by inter– and intra–molecular

151 hydrogen bonds and van der Waals forces of attraction *i.e.,* approximately 20–300 cellulose

152 chains are clustered to create microfibrils with an hydrophobic interior as well as hydrophilic

153 exterior structure and the bundle of microfibrils generate cellulose fibres (Agbor et al., 2011;

154 Bajpai, 2016a).

155   Table 1.   Compositions of various sources of LCB materials.

156

LCB material sources	Major chemical compositions			Refs.
	Cellulose (%)	Hemicellulose (%)	Lignin (%)	
Grasses and Weeds (Herbaceous crops)				(Dharmaraja et al.,
Amur silver–grass	42.00	30.15	7.00	2019; Mankar et al.,
Bamboo	41.80	18.00	29.30	2021; Moodley et al.,
	46.50	18.80	25.70	2020; Sankaran et
	26–43	30.00	21–31	al., 2020)
Bamboo leaves	34.14	25.60	35.00	
Bermuda grass	32.40	24.80	20.33	
	47.80	13.30	19.40	
Big bluestem	29.00–37.20	20.50–25.80	17.10–23.80	
Coastal Bermuda grass	25.00	35.70	6.40	
Crofton weed stem	37.60	22.40	16.40	
C. odorata (Siam weed)	41.00	17.30	20.70	
Elephant grass	47.12	36.01	11.50	
Eichhornia crassipes	18.20	48.70	3.50	
Ensiled grass	37.90	27.30	9.70	
Hemp	53.86	10.60	8.76	
	68.00	15.00	10.00	
Lantana camara	45.10	17.00	27.30	
Meadow grass	41.28	28.14	30.14	
Napier grass	47.00	31.00	22.00	
	45.70	33.70	20.60	
Naturally hay	44.90	31.40	12.00	
Orchard grass	52.30	42.90	6.60	
Reed	49.40	31.50	8.74	
	39.50	29.80	24.00	
Rye	42.83	27.86	6.51	
Saccharum spontaneum	45.10	22.80	24.40	
Silage	39.27	25.96	9.02	
Smooth brome grass	49.80	41.90	7.60	
Sunflower	34.06	5.18	7.72	
Switchgrass	26.80–37.50	22.40–28.80	13.20–22.50	
Szarvasi–1	37.85	27.33	9.65	
Tall fescue	23.40–26.40	18.20–20.40	10.90–14.80	
Verge grass	30.70	15.60	14.10	
Hardwood				(Ashokkumar et al.,
Acacia pruning	49.00	13.00	32.00	2022; Dharmaraja et
American sycamore	37.20–41.80	17.60–19.60	25.00–27.30	al., 2019; Hassan et
				al., 2018; Kumar et
				al., 2020, 2019)
Aspen	52.70	21.70	19.50	

Beech wood	40.00	23.00	21.00	
Black locust	39.30–42.60	16.60–18.90	24.40–28.60	
Cherry wood	46.00	29.00	18.00	
Eucalyptus	44.90	28.90	26.20	
	46.60–50.30	12.70–14.40	26.90–28.20	
Eastern red cedar	40.30	35.90	8.50	
Hybrid polar	403.0–47.30	16.60–22.60	15.50–16.30	
Oak	43.20	21.90	35.40	
Poplar	46.00	16.70	26.60	
Rubber wood	39.56	28.42	27.58	
Willow	42.40–45.30	20.60–22.90	16.90–18.90	
Softwood				(Anu et al., 2020;
Beech wood	44.20	33.50	21.80	Dey et al., 2022;
Fir	45.00	22.00	30.00	Dharmaraja et al.,
Hemlocks	47.50	22.00	28.50	2019; Hassan et
Japanese cedar	52.70	13.80	33.50	al., 2018; Yadav et
Pine wood	38.20	24.10	34.40	al., 2020)
	45.60	24.00	26.80	
	46.40	8.80	29.40	
	42.00–50.00	24.00–27.00	20.00	
Pinus armandii Franch	48.40	17.80	24.10	
Spruce wood	24.70	10.20	35.00	
	29.00	30.00	22.80	
	43.00	29.40	27.60	
	45.50	22.90	27.90	
Sawdust				(Ashokkumar et al.,
Gmelina arborea sawdust	23.00	–	23.30	2022; Ummalyma et
Salvadora oleoides saw dust	24.00	–	21.80	al., 2019)
Willow sawdust	35.60	21.50	28.70	
Agricultural and food processing industry wastes				(Agbor et al., 2011;
Apple pomace	8.810	5.440	2.98	Amini et al., 2021;
Acacia pruning	44.90	13.00	32.00	Ashokkumar et al.,
Almond shell	27.00	30.00	36.00	2022; Dharmaraja et
Bamboo	46.50	18.80	25.70	al., 2019; Haldar and
	45–50	18–20	23.00	Purkait, 2021;
	26–43	15–26	21–31	Hassan et al., 2018;
Bamboo leaves	34.14	25.55	35.03	A. Khan et al., 2022;
Banana waste	13.20	14.80	14.00	New et al., 2022; Raj
Banana peel	12.17	10.19	2.88	et al., 2022;
	11.45	25.52	9.82	Sewsynker–Sukai et
Barley straw	35.40	28.70	13.10	al., 2020; Usmani et
	45.00	38.00	19.00	al., 2020; Yoo et al.,
	36.00–43.00	24.00–33.00	6.30–13.10	2017)
Barley hull	34.00	36.00	13.80–19.00	
Carrot pomace	28.00	6.70	17.50	
	10.01	5.73	2.50	

Citru peel	20.80	17.20	8.90
Chestnut shells	20.50	15.16	47.01
Chili post–harvest residue	39.90	17.80	25.30
Coconut coir	44.20	22.10	32.80
Coffee grounds	33.10	30.03	24.52
	12.40	39.10	23.90
	11.60–33.10	37.20–41.00	22.20–25.60
Coffee pulp	35.00	46.30	18.80
Com cobs	41.00	31.00	12.00
	45.00	35.00	15.00
	33.70–41.20	31.90–36.00	6.10–15.90
Corn stalks	50.00	20.00	30.00
	35.00	28.00	17.00
	35.00–39.60	16.80–35.00	7.00–18.40
Corn stover	38.40	22.90	20.10
	39.00	19.10	15.10
	37.00	22.70	18.60
	43.97	28.94	21.82
	34.50	27.70	16.50
	37.50	22.40	17.60
	41.70	20.50	18.00
	43.90–30.60	19.10–28.90	16.70–21.80
Cotton seed hairs	80–95	5–20	0.00
Cotton gin	20.00	9.10	17.60
Cotton stalk	67.00	16.00	13.00
Cucumber pomace	16.13	4.33	4.51
Extracted olive pomace	19.00	22.00	40.00
Giant reed stalk	33.00	18.50	24.50
Groundnut shell	37.00	18.70	28.00
Hazel branches	30.80	15.90	19.90
Hazelnut shell	42.10	28.20	25.20
	30.00	23.00	38.00
	25.20	28.20	42.10
Hybrid poplar	44.00	20.00	29.00
	40.00	22.00	24.00
Lemon peel	23.10	8.09	7.60
	12.72	5.30	1.73
Mango peel	9.19	14.51	4.25
Miscanthus	35.00–40.00	16.00–20.00	20.00–25.00
Orange peel	9.21	10.50	0.84
	11.93	14.46	2.17
	13.61	6.10	2.10
Palm oil frond	37.32	31.89	26.05
Peanut shell	48.00	3.00	28.00
Pineapple peel	12.00	6.50	11.00
Pine nut shell	31.00	25.00	38.00

Pistachio shell	15.20	38.20	29.40
Rice husk	37.10	29.40	24.10
	40.00	16.00	26.00
Rice straw	35.80	21.50	24.40
	41.00	21.50	9.90
	38.00	32.00	12.00
	38.14	31.12	26.35
	41–57	33.00	8–19
	39.00	15.00	10.00
	32.10	24.00	18.00
Sorghum straw	26.93	32.57	10.16
Sorghum straw	26.93	32.57	10.16
Sugar tops	43.00	27.00	17.00
Sugarcane bagasse	35.00	35.80	16.10
	43.10	31.10	11.40
	31.90–43.40	12.20–25.50	23.10–27.60
Sugarcane peel	41.11	26.40	24.31
Sweet sorghum bagasse	27.30	13.10	14.30
Switch grass	31.00	20.40	17.60
	31.00	22.00	18.00
	45.00	31.40	12.00
Tomato pomace	8.60	5.33	5.85
Tobacco chops	22.00–30.00	15.00–20.00	15.00–25.00
Walnut shell	53.50	20.40	23.30
	50.30	22.40	23.90
Water hyacinth	24.50	34.10	8.60
Wheat straw	43.40	26.90	22.20
	38.20	21.20	23.40
	38–45	15–31	12–20
	36.60	24.80	14.50
	44.00	29.60	10.40
	41.30	30.80	7.70
	33.00	23.00	17.00
	30.00	50.00	15.00

157

158   The long chain polymers that are packed into macrofibrils and these macrofibrils are
159   covered by hemicellulose and lignin contents. The formed fibrils are highly microcrystalline
160   (50–90 %) with linear structure however, 10–45 % existence of the amorphous regions is due to
161   random orientation of structural units. The formation of fermentable simple D–glucose unit from
162   the cellulose *via* either mineral acid or enzymes break the (β–1–4)–glycosidic bonds (Bajpai,
163   2018, 2016a; Bhatia et al., 2020; Lorenci Woiciechowski et al., 2020; Mankar et al., 2021). The
164   second most abundant of LCB materials are made of hemicelluloses [$(C_5H_{10}O_5)_m$] with ~15–35

165 % of the total biomass sources. It is comprised of highly amorphous, branched short side chains,

166 and heteropolysaccharide polymeric nature with C_5 (β–D–xylose &α–L–arabinose) and C_6 (D–

167 glucose, D–mannose & D–galactose) sugar units, sugar acids (α–D–4–O–methyl–D–glucuronic,

168 α–D–galacturonic and α–D–glucuronic) and a tracer amount of α–α–L–fucose, L–rhamnose,

169 acetyl groups and uronic acids (Bajpai, 2018, 2016a; Bhatia et al., 2020; Lorenci Woiciechowski

170 et al., 2020; Mankar et al., 2021; Yousuf et al., 2019). The backbone of hemicellulose structure is

171 fashioned through heteropolysaccharide polymer chains of C_5 and C_6 monomeric sugar units

172 with short lateral branches. The sugar units are linked through β–1,4–D–glucosidic bonds, which

173 all through make the outer surface of the cellulose is more rigidity and provide more amorphous

174 matrix as well. The lignin [$(C_{10}H_{11}O_{3.5})$; of ~ 10–20 % the total LCB sources is the third most

175 rich organic heteropolymeric compound after the cellulose and it is liable for high hydrophobic

176 as well as rigidity in structural nature. It binds cellulose to hemicellulose in the plant cell wall

177 like sandwich bind, it also confers a rigid, impermeable, resistance to any microbial attack as

178 well as oxidative stress. Lignin is a very complicated 3D amorphous complex with polyphenol

179 structural feature, due to high molecular weight and degree of cross–linked polymers of

180 phenylpropane monomeric units (Brandt et al., 2013; Hosseini Koupaie et al., 2019; Zoghlami

181 and Paës, 2019). The biopolymeric structure of lignin moiety contains a cross–linked

182 phenylpropanoid units and has widely been utilized as the key chemical precursors as well as

183 alternative to low–cost renewable feedstock materials. Generally, the lignin is an amorphous

184 heteropolymeric network with hydroxylated and methoxylated phenylpropanoid monomeric or

185 monolignol units namely, p–coumaryl alcohol or $para$–hydroxyphenyl (H–unit), coniferyl

186 alcohol or guaiacyl (G–unit) and sinapyl alcohol or syringyl (S–unit) (Nimmanterdwong et al.,

187 2021; Yousuf et al., 2019; Zoghlami and Paës, 2019). Furthermore, the relative amount of

188 H/G/S–units present in the various biomass plant materials are 5, 95 and 0 % for softwoods

189 (pinus and spruce), 0–8, 25–50 and 45–75 % for hardwoods (birch, beech and aspen) and 5–35,

190 35–80 and 20–55 % for grasses, respectively (Li et al., 2016). The existence of the above

191 interlinked ether (C–O–C) and C–C bond linkages such as β–O–4, α–O–4, β–5, 5–5, β–1and β–β

192 of lignin provide a highly heterogeneous nature with 3D complex polymeric structure. This

193 linkages have been catalyzed to produce variety of high value added aromatic by–products such

194 as ethylbenzene, guaiacol, p–hydroxyl acetophenone, $etc.,$ (Garedew et al., 2021). Furthemore,

195 lignin showed physically very limited polysaccharide accessibility and also binds the different

196   components of LCB together, thus making it as insoluble water components. Also, it plays a role

197   as physical barrier that blocks the access of enzymes to cellulose *i.e.,* lignin acts as key obstacle

198   to enzymatic and microbial hydrolysis of LCB materials.

199

200   **3.   Various LCB pretreatment methods**

201

202   In general, the effectiveness of LCB pretreatments accomplished by economic and

203   environmental feasibilities *i.e.,* to employ an efficient LCB pretretamnet technology should be

204   attentive in vein of their cost–reduction, environmental concerns, and sustainability, that leads to

205   increase the specific surface area and porosity, cellulose digestibility by disrupting the rigid

206   carbohydrate–lignin matrix, reduction of the particle size, removal of hemicellulose/lignin

207   content, *etc.*, which resulting an high percentage of simple sugar unit recovery after enzymatic

208   hydrolysis (Ashokkumar et al., 2022; Raj et al., 2022). Hence, the breakingdown of

209   hemicelluloses as well as lignin contents present in the plant cell walls through various

210   pretreatment technologies, before the enzymatic digestion process leads to enhance the

211   generation of simple fermentable sugar units into biofuels and biocompounds production from

212   LCB materials (Shirkavand et al., 2016). The effective LCB pretreatment process should possess

213   (i) formation of high percentage of fermentable sugar unit contents during downstream

214   processing, (ii) pretreatment tools applied for all types of LCB materials, (iii) recovery of lignin

215   and hemicellulose moieties for consequent combustion process, (iv) minimum or low generation

216   of co–products or inhibitors for subsequent pretreatment process, (v) efficient recovery of lignin

217   content for further conversion or production into high value added biocompounds, (vi) avoiding

218   the degradation of pentoses derived from hemicellulose moieties, (vii) minimization of the cost

219   effective pretreatment process by applying eco–friendly chemicals or solvents, moderate size of

220   reactors as well as minimizing the energy consumption (both heat and power) routes, *etc.,* (Cheah

221   et al., 2020; Shirkavand et al., 2016). Recently, the most advanced LCB pretreatment

222   technologies are typically categorized into four methods namely physical, chemical, physico–

223   chemical, and biological (Ashokkumar et al., 2022; Ummalyma et al., 2019).The key objective

224   of physical pretreatment includes the utilization of mechanical operations including grinding,

225   ball milling, screw pressing, soaking or pelleting, mechanical extrusion, freezing, microwave,

226   ultrasonication *etc.,* which reduce the crystallinity and particle size of LCB materials, that leads

227 to increase the surface area and degree of polymerization (DP) of LCB into fast digestion as well

228 as solubilization (Hendriks and Zeeman, 2009; Shirkavand et al., 2016; Yadav et al., 2020). In

229 addition, there is no formation of toxic materials or inhibitors, it is the chief feature of these

230 technologies (Shirkavand et al., 2016). The mechanical grinding operations mainly reduce the

231 particle size, DP and crystallinity of LCB, which further increased the rate of enzymatic

232 hydrolysis process and the generation of biofuels and biocompounds (Chandel et al., 2022). The

233 pelleting or soaking methods, utilization of mineral acid/base or alkaline solution improves the

234 enzymatic LCB digestibility to reduce the cellulose crystallinity and also upgrades the

235 delignification rate. By applying ball as well as wet disk milling operations to LCB materials,

236 there is generation of high yield on celluloses and xylose compounds after the successful

237 enzymatic hydrolysis but such operations consume very high energy (Shirkavand et al., 2016).

238 During the mechanical extrusion operation to LCB materials, face shearing, mixing as well as

239 heating, lead to a sudden reduction of particle size in DP of LCB. However, using the microwave

240 or ultrasound or pulsed electric field process, the LCB materials are treated with high energy

241 EMR (electromagnetic radiation or wave) for a short time period, it degrades the cellulose and

242 hemicellulose fraction structure *i.e.,* such kind of operation more effectually removes

243 hemicellulose and lignin moieties present in LCB and also it interrupts the ester and ether

244 linkages present in both cellulose and lignin moieties. Then only it can readily undergo

245 hydrolysis process with generation of high yield efficiency for simple fermentable sugar units,

246 but such methods are cost–intensive (Chandel et al., 2022; Shirkavand et al., 2016; Singh et al.,

247 2022; Yadav et al., 2020). The cavitational effect on principle of ultrasound radiation technology

248 is widely being applied on LCB pretreatment process that leads to breakdown the lingnin α–O–4

249 and β–O–4 linkages. Recently, a novel freezing and thawing approaches are widely being

250 utilized in physical pretreatment process of LCB materials (Singh et al., 2022). But, one major

251 drawback for utilizatilation of the physical pretreatment is the energy consumption (Tu and

252 Hallett, 2019). Furtrher, this physical tehnology is not suitable for large–scale industrial process,

253 due to its high energy requirements. The chemical pretreatment methods, including acid

254 hydrolysis (mild & concentrated mineral HCl, H_2SO_4, HNO_3, *etc.,* and organic oxalic, maleic,

255 succinic acids, *etc*), alkaline or base hydrolysis (KOH, NaOH, Na_2CO_3, CaO, $CaCO_3$/$Ca(OH)_2$,

256 NH_3, *etc*), organic solvents and greener ionic liquid as well as deep eutectic solvent methods are

257 broadly employed to breakdown directly the cellulose and hemicellulose fractions in LCB

258 materials and hydrolyses the bonds that leads to generate the monomeric C_5 and C_6 sugar units,

259 which are convereted into high value added biocompounds and biofuels (Bhatia et al., 2020;

260 Kant Bhatia et al., 2022; Solarte–Toro et al., 2019; Tian et al., 2018).

262 Generally, acid pretreatments are extensively employed for LCB pretreatment

263 technologies, due to its low cost and high efficiency to hydrolyse the hemicellulose contents into

264 monomeric fermentable sugar units without dissolving lignin moieties. But, the major drawback

265 for this hydrolysis method is the formation of high value added lignin by–products like furfurals

266 (FF), 5–hydroxymethylfurfural (5–HMF) and phenolic acids, which are more corrosive as well

267 as microbially toxic intermediate inhibitor compounds, high acidic wastewater generation, *etc.,*

268 thereby, need to recovery as well as neutralization of acids (Kant Bhatia et al., 2022). While

269 applying this method to LCB materials, the common disadvantages are extremely effective at

270 deconstruction, the production of toxic or inhibitor compounds, carbohydrate loss and high cost

271 (Anu et al., 2020; Shirkavand et al., 2016).

273 In addition, the combined physical and chemical pretreatments in physico–chemical

274 technologies such as ammonia–based (AFEX : Ammonia fiber/freeze explosion, ARP :

275 Ammonia recycle percolation, and SAA : Soaking aqueous ammonia), supercritical fluids (SCF)

276 explosion, wet oxidation, steam explosion and liquid hot water (LHW) pretreatments are

277 effectively utilized on different types of LCB materials towards the production of fermentable

278 simple sugar contents. Also the deconstruction of LCBs, using such technologies is more

279 predictable with immediate discharge of high pressure that leads to breaking down of the

280 complex network structure of LCB materials within a short period of time. Further, the biological

281 pretreatment techniques are generally more superior than other pretreatment process (Anu et al.,

282 2020; Dey et al., 2022; Hassan et al., 2018; Yadav et al., 2020) because these kind of methods

283 offer various advantages such as low capital cost & energy, decrease in the dependence on

284 chemicals, minimum formation of inhibitors. But the main disadvantages are the low hydrolytic

285 rate and requirement of very long pretreatment times. This pretreatment mainly involves the

286 utilization of microbes such as white rot, brown rot and soft–rot fungus or metabolites from

287 enzymes such as peroxidase, hydrolases, ligases, laccases, oxidoreductase, isomerases, *etc.*, are

288 mostly utilized in these pretreatment processes due to their special lignolytic and delignification

289   properties. They are playing a vital role to degrade hemicellulose and lignin contents and also

290   depolymerization of LCB, outside plant cell wall *i.e.,* delignification and saccharification of LCB

291   components, before the enzymatic hydrolysis (Anu et al., 2020; Dey et al., 2022; Hassan et al.,

292   2018; Yadav et al., 2020). Moreover, the effective LCB pretreatments are also affected by

293   various issues of physical and chemical properties such as cellulose crystallinity, lignin content,

294   the existing linkages between cellulose and lignin (Ashokkumar et al., 2022; Ummalyma et al.,

295   2019). Hence, a simple or particular LCB pretreatment technology does not provid an efficient

296   and expected LCB degradability results. So, the combined pretreatment processes, which are

297   integrating two or more pretreatment tehnologies from the above mentioned four methods

298   showed more effective and upgraded LCB pretreatment than application of single process

299   (Ummalyma et al., 2019).

300

301   **3.1.   Greener pretreatment approaches**

302

303   Currently, the concept of 12 principles of green chemistry or greener concepts have

304   widely been studied and also utilized as an emerging pretreatment process to the challenge of

305   upgrading any type of LCB materials feasiblly to biorefinery approach into valuable compounds.

306   Various LCB pretreatment technologies are already available, but some of them are greenest as

307   well as economical technologies mainly like Ionic liquids (ILs), Deep eutectic solvents (DESs),

308   steam explosion (SE) or steram pretreatment (SP), supercritical carbon dioxide explosion (*Sc–*

309   CO_2), Co–solvent enhanced lignocellulosic fractionation (CELF), *etc.,* are well proven that the

310   formation of low or no inhibitors, enhanced conversion rate of complex polysaccharides into

311   fermentable simple sugar units generation and other value added biofuels and biocompounds

312   formation from LCB materials in large scale industrial processes (Hassan et al., 2018; Sharma et

313   al., 2022; Usmani et al., 2020). Recently, the state–of–art in the development of novel greener

314   technologies showed chief promising as well as convincing methods in the field of LCB

315   pretreatments. The selected greener approaches are currently being employed for LCB

316   pretreatment methods and are summarised in Table 2.

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320   Table 2.   Comparison of various LCB pretreatment technologies with their effects, advantages and disadvantages [Adopted from
321   modified Refs. (Ashokkumar et al., 2022; Bajpai, 2020, 2016c, 2016b; Chandel et al., 2022; Dharmaraja et al., 2019;
322   Elgharbawy et al., 2016; Hassan et al., 2018; Moodley et al., 2020; Raj et al., 2022; Salakkam et al., 2019; Sankaran et
323   al., 2020; Thanigaivel et al., 2022)].

Pretreatment methods	Effects	Advantages	Disadvantages
Physical pretreatment			
Mechanical (Ball & Hammer milling, Crushing, Cutting, Shredding)	Reduce the particle size and disrupt the crystallinity	Control of final particle size, easy handling, less waterconsumption, free from chemical intake, increased surface area, low production cost	High energy consumption than inherent biomass energy, low release of sugar content, commercial feasilbility is very less, inability to remove lignin which restricts the access of the enzymes to cellulose and inhibit cellulases
Irradiation (Microwave and Ultrasound)	Swelling andfragmentation oflignocellulosicmaterial	Fast heat transfer, shortreaction time, energyefficient, cheap and generate less / no pollution, increased porosity, highly efficient at batch scale, dissolve extractives with heating	Low penetration of radiationin bulk products, distribution of microwavepower around of LCB dueto non–homogeneous material, high energy consumption than inherent biomass energy, low release of sugar content, commercial feasilbility is very less
Chemical pretreatment			
Acid hydrolysis (using dilute or concentrated acids, organic acids)	Lignin cellulose and hemicellulose fractionate	Enzymatic hydrolysis not required the acid, hydrolyzes the hemicellulose into xylose and other sugars, alters lignin structure, increase in porosity, increased enzymatic hydrolysis, commercial feasible, high enzymatic yield, increased cellulose crystallinity, short retention time	Concnetrated acid process is corrosive and toxic, formation of inhibitors at low pH& pseudo lignin as by–products, high cost, equipment corrosion,formation of toxic substances at higher severity, need acid neutralization, toxin formation at higher severity, requirement high metallurgy, pseudo lignin formation, cellulose crystallinity enhancement
Base or Alkaline hydrolysis	Lignin and hemicellulose removal	Reduce the absorption of cellulose due to efficient lignin removal, low cost, utilize lower temperatures and	Generates inhibitors, long residence time required, less effective as lignin content of the biomass increases, treatment of a large

15

		pressures than other pretreatment technologies, less sugar degradation compared with acid processes, caustic salts can be recovered and/or regenerated, complete removal of lignin and partial removal of hemicellulose, decrease the degree of polymerization	amount of salts becomes a challenging issue for alkaline pretreatment, need large amounts of water for washing, low digestibility in softwoods, high dose of chemical requirement, additional requirement of neutralizing agents, slippery nature of pretreated biomass, xylo oligomers formations, requirement high metallurgy
Ionic liquids (ILs) and Deep eutectic solvents (DESs)	Celluloseprecipitation, effective depolymerizes lignin by cleavage of β–O–4 linkage, hemicellulose fractionation and lignin removal	Green solvent, biodegradable and biocompatible, working under mild reactionconditions, low vapor pressure, high thermal stability and polarity, eco and environmental friendly manner, low volatility and need low vapor pressure designer solvent,high lignin and hemicellulose solubilization, reduced crystallinity, high pore size distribution, cellulose crystal structural transformation, no inhibitor formation, suitable for small scale, recyclable green in nature, higher sugar release during hydrolysis	High cost of ILs& DESs, recycling process is highly challenging, high complexity of purification and synthesis, strong tendency to denature enzymes, toxic to enzymes and yeast,commercially not applicable, Poor stability under higherpretreatment temperatures
Organosolv	Lignin removal and hemicellulose fractionate	Formation of a high purity of lignin, highly selective for lignin solubilization without chemical alteration of chemical structure, increases overall surface area, reduces biomass crystallinity, recyclable at optimized conditions	High capital cost, need to separate solvent &washing step, ease of recovery, toxicity, safety (low vapor pressure) and environmental concerns are still challenging for scale–up utilizations, the need for pressure reactors, temperature control and process optimization are major concerns

Physico–chemical pretreatment

Steam explosion	Particle size reduction, partial hydrolysis of hemicellulose, lignin	Less usage of water, no chemical uses, low environmental impacts, limited use of chemicals, requires low	High equipment cost, incomplete destruction of lignin–carbohydrate matrix, destruction of a portion of the xylan in hemicellulose,

	removal, lignin softening, particle sizereduction	energy input with no recycling or environmental cost	decreases the overall saccharification yields, release inhibitory by–products, much less effective for softwood
Liquid hot water (LHW)	Partial hydrolysis of hemicellulose, lignin removal	Does not require washing, chemical recovery, ordetoxification steps, minimum formation of degradation products at lower temperatures, eliminates the need for a final washing step or neutralization, low cost of the solvent is also an advantage for large–scale application	High water consumption andenergy input, amount of solubilized product is higher, while the concentration of these products is lower compared to steam explosion, more energy demanding because of the large volumes of water involved, mainly removes hemicellulose
Ammonia–based method (AFEX : Ammonia fiber/freeze explosion, ARP : Ammonia recycle percolation, and SAA : Soaking aqueous ammonia)	Decreases the crystallinity and lignin removal	Low formation of by–products, increases accessible surface area, removes lignin and hemicellulose, reduce the lignin fraction, short retention time,minimum formation of inhibitory by–products for downstream process, decrystallization of cellulose, high selectivity for reaction with lignin, an efficient and selective delignification method	Not suitable for lignocellulosic biomass with high lignin content, costly, ineffective in the pretreatment of high lignin–containing lignocellulosic biomass, cost of ammonia basically drives the process and its application on large scale, environmental concerns with the stench of ammonia also have a negative impact on pilot and industrial scale applications
SPORL	Lignin removal and Hemicellulose fractionate	Low formation of inhibitors, energy–efficient, reduces the absorption by sulfonation of cellulose	High cost of chemical recovery
Biological pretreatment			
Microorganisms and enzymes	Lignin,hemicellulose, and cellulosedegradation	Selective degradation oflignin, hemicellulose, andcellulose, low energy required, chemical–free method, complete degradation of lignin, environmentallyfriendly	Long pretreatment time, low sugar release, hydrolysis rate is low

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3.1.1. Novel green solvent–based ILs and DES pretreatments

Ionic liquids (ILs) or designer solvents are an alternate potent greenermolten salts, which are formed by the combination of bulky H–doanting organic cations like imidazolium, pyridinium, pyrrolidinium, aliphatic ammonium, alkylated phosphonium, sulfonium, *etc.* with suitable H–bond accepting organic/inorganic anions like halides, acetates, tetrafluoroborate, hexafluorophosphate, dicyanamide, *etc* (Brandt et al., 2013, 2011; Raj et al., 2022; Usmani et al., 2020; Yoo et al., 2020). In addition, ILs are widely employed in several areas like catalysis, biocatalysis, analytical and electro–chemical applications, *etc.,*because they showed their unique physico–chemcial properties such as very high chemical and thermal stability, moderate boiling and melting (lower than 100 °C) points, high recyclability as well as reusability nature, and eco–friendly nature, *etc* (Agbor et al., 2011; Amini et al., 2021; Ashokkumar et al., 2022; Chavan et al., 2022; Haldar and Purkait, 2021; Hassan et al., 2018; M. U. Khan et al., 2022; Usmani et al., 2020). Generally, the imidazolium based ILs are widely employed in greenest LCB pretreatment approach because, the molten organic IL salts shows some merits such as very low vapour pressure, high viscosity, non–corrosive, non–flammable, non–toxic, excellent biodegradability, high thermo–chemical stability, *etc.,* (Agbor et al., 2011; Usmani et al., 2020). ILs effactually can dissolve cellulose, hemicellulose and lignin moieties in LCB *via* breaking down of the linkages *viz* intra– as well as inter–molecular hydrogen bonds existing in macrofibrils of cellulose fibers *i.e.*, disruption of the LCB structural network leads to decrease the lignocellulosic crystallinity, which obviously facilitates enzyme access to cellulose and hemicelluloses for enhancing the bioconversion of LCB into fermentable sugar units and high value added biofuels/biocompounds (Amini et al., 2021; Ashokkumar et al., 2022; Haldar and Purkait, 2021; Hassan et al., 2018; M. U. Khan et al., 2022; New et al., 2022; Usmani et al., 2020). A schematic representation of ILs LCB pretreatment process is depicted in Fig. 1.

Some of the important ILs like [Amim]HCOO: 1–Allyl–3–methylimidazolium formate, [Amim]Cl: 1–Allyl–3–methylimidazolium chloride,[AMMorp] OAc: N–allyl–N–methylmorpholinium acetate, [BDTA] Cl: benzyldimethyl (tetradecyl)ammonium chloride,[Bmim]OAc: 1–Butyl–3–methylimidazolium acetate, [Bmim]Br: 1–Butyl–3–methylimidazolium bromide, [Bmim]Cl: 1–Butyl–3–methylimidazolium chloride, [Bmim]I: 1–

357 Butyl–3–methylimidazolium iodide,[Bmim]MeSO$_4$: 1–Butyl–3–methylimidazolium

358 methylsulfate, [BmPy]Cl: 1–Butyl–3–methylpyridinium chloride, [C$_4$C$_1$im][MeSO$_4$]: 1,3–

359 dimethylimidazoliummethyl sulfate, [C$_4$C$_1$im][HSO$_4$]: 1–butyl–3–methylimidazolium

360 hydrogensulfate, [C$_4$Him][HSO$_4$]: 1–butylimidazolium hydrogen sulfate, [C$_4$C$_1$im]Cl: 1–butyl–

361 3–methylimidazolium chloride, [C$_4$C$_1$im][MeCO$_2$]: 1–Butyl–3–methylimidazolium acetate,

362 [Emim]OAc: 1–Ethyl–3–methylimidazolium acetate,[Emim]Cl: 1–Ethyl–3–methylimidazolium

363 chloride, [Hmim]CF$_3$SO$_3$: 1–Hexyl–3 methylimidazolium trifluoromethanesulfonate,

364 [Mmim]MeSO$_4$: 1,3–Dimethylimidazolium methylsulfate, [MBPcl]: 3–methyl–N–

365 bytylpyridinium chloride, [NMMO]: N–methylmorpholine–N–oxide monohydrate,

366 [N4444]OAc: Tetrabutylammonium acetate, [Py]OAc: Pyridinium acetate, [Py]For: Pyridinium

367 formate, [Py]Pro: Pyridinium propionate *etc.,* have widely been utilized for LCB pretreatment

368 methods (Amini et al., 2021; Haldar and Purkait, 2021; New et al., 2022).

369

370 Table 3 summarizes the solubilization yield (wt %) of cellulose and lignin moieties of

371 various LCB materials using ILs pretreatment. A mixture of ILs like [C$_4$C$_1$im][MeSO$_4$],

372 [C$_4$C$_1$im][HSO$_4$], [C$_4$Him][HSO$_4$], [C$_4$C$_1$im]Cl, [C$_4$C$_1$im][MeCO$_2$], *etc.,* combined with water

373 are effectively utilized by LCB pretreatment of various biomasses, including mainly *miscanthus*,

374 pine, willow, maple wood, switchgrass, and oak. Moreover, the ILs can be recovered and reused

375 after each cyclic pretreatment through different methods such as reverse osmosis (RO) and ion

376 exchange or salting out processes (Usmani et al., 2020). After the LCB pretreatment by ILs, the

377 separation of the liquid as well as solid parts are associated with some loss of LCB sugars, so a

378 combination of saccharification, deconstruction and then enzymatic fermentation processes are

379 probably required to reach the ultimate way for reducing the cost of IL operation. Brandt *et al.,*

380 studied the pretreatment of *Miscanthus giganteus*, pine (*Pinus sylvestris*), and willow (*Salix

381 viminalis*) biomasses with two ILs namely 1–butyl–3–methylimidazolium hydrogen sulfate

382 [Bmim][HSO$_4$]$^-$ and 1–butyl–3–methylimidazolium methyl sulfate [Bmim][CH$_3$SO$_4$] (Brandt et

383 al., 2011). It showed that >9 0% recovery of glucose yields due to the presence of certain

384 anions, which are the predominant sources in lignin dissolution with high recovery of cellulose

385 moieties for LCB materials.

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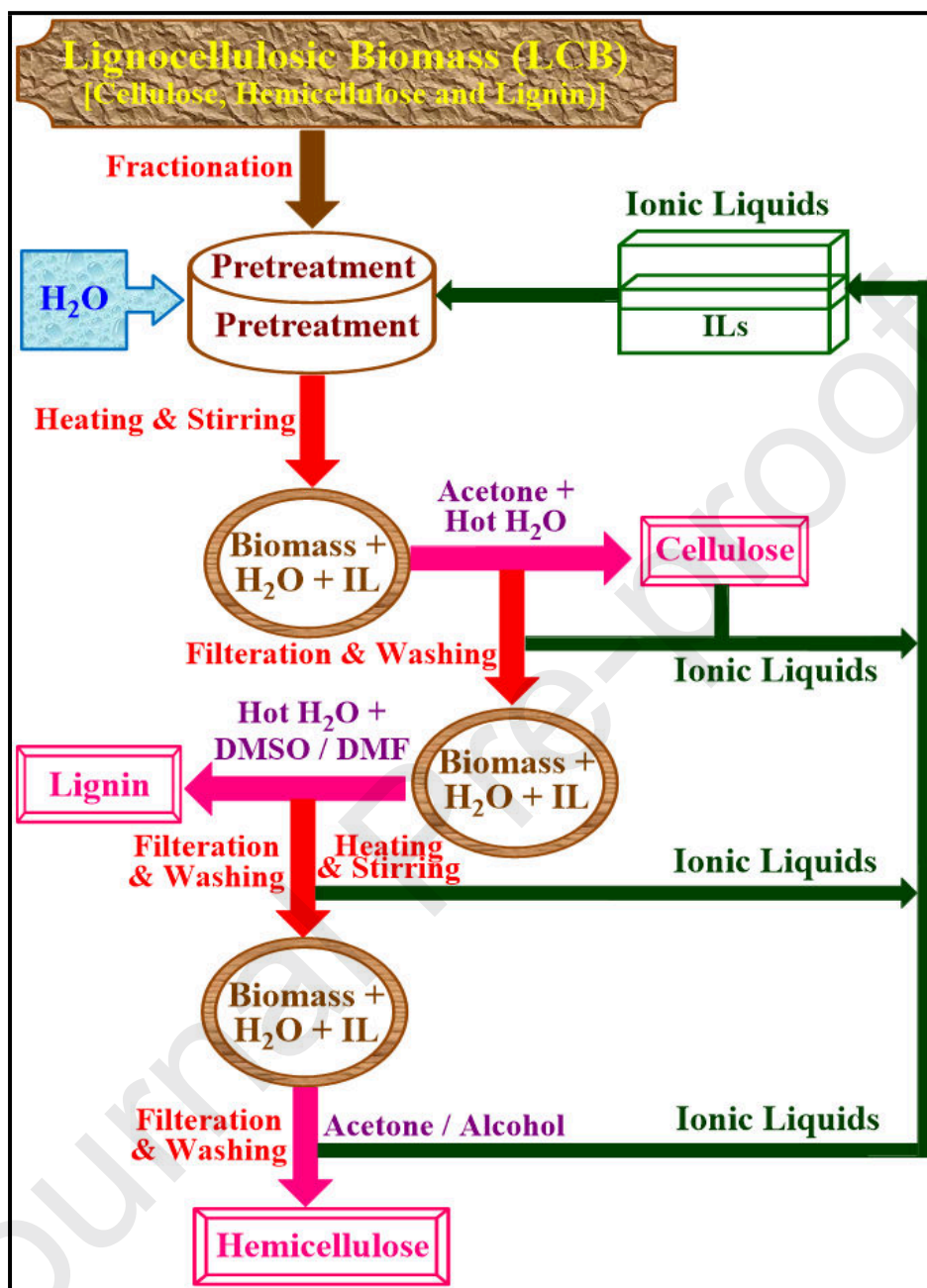
389

390   **Fig. 1.**   LCB pretreatment process with ILs [Adopted and modified Ref. (Usmani et
391   al., 2020)].

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Table 3. Various LCB material sources under ILs pretreatement process and the yields of cellulose and lignin contents (wt %) [Adopted and modified Ref. (Usmani et al., 2020)].

LCB sources	IL solvent [a]	Experiment setup	Dosing (LCB / IL)	Residence Time	Temp. (ºC)	Soulbilization yield (wt. %)
For Cellulose						
Avicel® cellulose	[Bmim][Cl] + [Bmim][OAc] (3:2)	Round–bottom flask	–	4 h	80	23.40
Cotton linters	[Emim][OAc]	Arotray reactor	2 g / 50 ml	3 h	60	15.00
Pine Kraft Pulp	[Emim][OAc]	–	1 g/10 ml	3 h	60	12.00
Miscanthus Pulp	[triethylammonium][HSO$_4$]	Convection	1 g/10 g	8 h	120	41.00
Pine Pulp	[triethylammonium][HSO$_4$]	Convection	1 g/10 g	8 h	120	38.00
Spruce	[Bmim][Cl]	Whirlpool mixer	1 g/20 g	1 h	120	94.10
Willow	[Bmim][Cl] + Na$_2$SiO$_3$	Whirlpool mixer	1 g/20 g	1 h	120	96.80
Soyabean straw	[Bmim][Cl]	Whirlpool mixer	1 g/20 g	1 h	120	96.50
Rice Straw	[Emim][OAc]–DMSO (1:1)	Preheated using oil bath	50 mg / ml	10 min	80	28.00
	[Emim][OAc]–DMA (1:1)				80	28.00
	[Emim][DMP]–DMSO (1:1)				80	24.00
For lignin						
Miscanthus Pulp	[triethylammonium][HSO$_4$]	Convection	1 g / 20 g	8 h	120	20.00
Pine	[Bmim][MeCO$_2$]	–	1 g / 10 g	22 h	120	26.23
Pine Pulp	[triethylammonium][HSO4]	Convection	1 g / 10 g	8 h	120	5.00
Pine Pulp (Indulin)	[Ch][OAc]	–	5 mg / g	3 h	90	28.00

Biomass	Ionic Liquid	Co-solvent	Reactor	Loading	Time	Temperature	Yield
	[BMPyr][N(CN)$_2$]						39.00
Pine Pulp (lignin sulfonate)	[Ch][OAc]	–		5 mg / g	3 h	90	33.00
	[BMPyr][N(CN)$_2$]						56.00
Coir	[1,4–Butylene [Bmim][HSO$_4$]	Glycol/H$_2$O]–	Stainless Steel Reactor	1 g / 30 ml	30 min	90	24.06 ± 2.65
Poplar	[1,4–Butylene [Bmim][HSO$_4$]	Glycol/H$_2$O]–	Stainless Steel Reactor	1 g / 30 ml	30 min	90	11.12 ± 3.34
Coconut Shell	[Bmim][OAc]		Heating Block (N$_2$)	10 mg / g	2 h	150	8.60
	[Emim][OAc]						10.30
Switchgrass	[Bmim][PF$_6$]	–		15 g / 135 g	3 h	160	65.00
Eucalyptus	[Bmim][OAc]	–		5 g / 100 g	30 min	120	16.97
Oil palm frond	[Emim][DEP]		Round–bottom flask	1 g / 10 g	4 h	90 oil bath	13.00 ± 0.50
Oil palm biomass	[Bmim][Cl]		Rotary Evaporator	1 g / 10 g	8 h	110	22.78 ± 1.47
Bamboo biomass	[Emim][OAc]	–		0.5 g / 10 g	2 h	90	24.30 ± 0.80
						110	19.00 ± 1.20
						130	17.90 ± 1.00

399
400 [a][Bmim][OAc]: 1–butyl–3–methylimidazolium acetate; [Bmim][PF$_6$]: 1–butyl–3–methylimidazolium hexafluorophosphate;
401 [BMPy][Cl]: 1–butyl–3–methylpyridinium chloride; [BMPyr][N(CN)$_2$]: 1–butyl–1–methylpyrrolidinium; [Ch][OAc]: Cholinium
402 acetate; DMA: Dimethylacetamide; DMSO: Diethyl sulfoxide; [Emim][DMP]: 1–Ethyl–3–methylimidazolium dimethyl phosphate;
403 [Emim][DEP]: 1–Ethyl–3–methylimidazolium diethyl phosphate.

404   Agnieszka *et al*., investigated the fractionation of *Miscanthus x giganteus* grass material

405   with low–cost and economically viable IL namely [TEA][HSO4]: triethylammonium hydrogen

406   sulfate at a mild temperature (120 °C) (Agnieszka et al., 2017). It showed an enhanced

407   solubilization of lignin (85 %) and hemicellulose (100 %) moieties, which are on further

408   subsequent enzymatic saccharification of regenerated cellulose yielded, 77 % of glucose units.

409   The techno–economic analysis suggested that the cost of ILs–derived LC biomass is about 13.71

410    $/kg (Bhatia et al., 2020). Furthermore, the main disadvantages of using ILs on LCB

411   pretreatment processes are (i) more viscous nature of ILs, (ii) most of the ILs are toxic for

412   cellulase i.e., negative effect on cellulase activity, (iii) high cost of imidazolium based ILs, (iv)

413   conventional recovery and purification process of ILs are so expensive. These are the key

414   considerations for the large scale industrial applications. Hence, the enhanced production of

415   simple sugar units from LCB materials assisted with ILs in an pilot–scale plant is still now

416   needed some optimization (Bhatia et al., 2020; Tian et al., 2018; Usmani et al., 2020).

417

418   Currently, the emerging of deep eutectic solvents (DESs) as a new generation of mild and

419   sustainable greener solvents for LCB pretreatment process has been introduced as promising as

420   alternatives to ILs for LCB pretreatment (Ahmed et al., 2022). Since they are not only sharing

421   most of the merits of traditional ILs, but also overcome many of their drawbacks (Sharma et al.,

422   2022). They are composed of two or three ionic compounds, which are capable of self–

423   association to form a eutectic mixture. Also, the major milestone advantages of using DESs in

424   LCB pretreatment process is its extensive physico–chemical properties, which are much similar

425   to ILs (Mankar et al., 2021). DESs are liquid compounds, consisting of two or more solid organic

426   mixture of HBA (Hydrogen bond acceptor) like quaternary ammonium halide salt, metal halides,

427   *etc.* with HBD compounds (Hydrogen bond donor) like amino acids, amines, carboxylic acids,

428   carbohydrates, urea, *etc* (Ahmed et al., 2022; Lugani et al., 2020). The most widely applied

429   DESs are choline chloride [(ChCl)] with some urea, glycerol, carboxylic acids and polyols. They

430   have widely been utilized in numerous fields like pharmaceuticals, bio–refineris, food

431   productions, *etc*. Also, DESs are more emphasized in large scale industrial pretreatment as it is

432   an economical as well as eco–friendly solvent for LCB pretreatment technique and also DESs are

433   20 % much cheaper than traditional ILs (Zhang et al., 2021). DES solvents are promising

434   alternatives to ILs due to their non–toxicity, low cost, environmentally friendly nature, low

435   volatility, wide liquid range, biodegradability, enzyme compatibility, *etc.,* (Lugani et al., 2020).

436   Moreover, they have shown as an effective bioconversion of LCB on bench–scale experimental

437   level. The recycling and reusability of DESs can also be increased its economic as well as

438   technical efficiencies for LCB pretreatment technology. The HBDs are having strong electron–

439   withdrawing groups that showing an effective as well as enhanced LCB pretreatment

440   performence, while HBD contains –OH or –NH$_2$ group that shows low or negative efficiency

441   results. Further, the strong acidic DESs are effectively removing xylan from LCB structure. As a

442   result, the cellulose content is available readily for enzymatic hydrolysis process, even while the

443   presence of lignin in LCB structure (Jędrzejczyk et al., 2019). DESs pretreatment on various

444   LCB bioconversions with their effects are summarized in Table 4. Generally, the applications of

445   DESs on LCB pretreatment showed more effective solubilization of lignin moieties than

446   hemicellulose and cellulose contents (Mankar et al., 2021). The presence of –OH groups in DESs

447   leads to generate strong H–bonding network with cellulose and also stabilizing the DES–

448   Cellulose system. Procentese et al., reported that the pretreatment of agro–wastes mainly such as

449   apple residues, potato peels, coffee silverskin, and brewer's spent grains with two DESs namely

450   choline chloride–glycerol and choline chloride–ethyleneglycol showed the high efficiency of

451   fermentable sugar production as compared to other pretreatments as well as ILs process

452   (Procentese et al., 2018). In addition, the glycerol–choline DES showed more effective LCB

453   pretreatment than ILs method for industrial process. But, the ultilization of DESs in large scale

454   industrial LCB pretreatment process is still need some optimized modifications.

455

456   **3.1.2. Steam expolsion pretreatment**

457

458   The steam explosion (SE) or autohydrolysis or steam pretreatment (SP) method has

459   extensively been studied as well as employed as one of the physico–chemical pretreatment of

460   LCB materials (Agbor et al., 2011; Bajpai, 2016c). In SP/SE process, initially the LCB materials

461   undergo some physical treatments such as chipping, grounding and/or simple raw

462   preconditioning and then pretreated with high pressurized (0.7–4.8 MPa) saturated steam for

463   several seconds to few minutes at high temperature (160–240 ^{o}C).

464

465

466 Table 4. Various LCB material sources with DESs associated pretreatement process and their effects [Adopted and modified
467 Ref. (Lugani et al., 2020)].

LCB resource	Deep eutectic solvent	Pretreatement conditions	Effect on saccharification
Corn stover	Choline chloride–Formic acid	130°C, 2h, solid loading (5% w/v)	Glucose yield: 99% Lignin removal: 23.8%
Corncob	Choline chloride–Imidazole	115°C, 15 h, solid to liquid ratio (1:16, w/v)	Glucose yield: 94% Xylose yield: 84%
Eucalyptus saw dust	Choline chloride–lactic acid	110°C, 6 h, solid loading (10%, w/v)	Hydrolysis yield: 94.3% Delignification 80%
Lettuce residue	Choline chloride–glycerol	150°C, 16 h, solid:liquid ratio (1:16, w/v)	Glucose yield: 94.9% Xylose yield: 75.0%
Oil palm empty fruit bunch	Choline chloride–lactic acid	120°C, 3 h, solid to liquid ratio (1:10, w/v)	Reducing sugars yield: 20.7%
	Choline chloride–Urea	110°C, 1 h, solid to liquid ratio (1:5, w/v)	Glucose yield: 66.33 mg/ml
Oil palm fronds	Choline chloride–Urea–CuCl$_2$	120°C, 30 min, solid loading (10%, w/v)	Xylose yield: 14.76 g/L
Rice straw, rice husk, and wheat straw	Choline chloride–Oxalic acid–n–butanol	120°C, 1 h, solid loading (15%, w/v)	Delignification:50%
Rice husk	Ethylene glycol–choline chloride	160°C, 4 h, solid loading (4%, w/v)	Reducing sugar yield: 0.74 mg/mL
Rice straw	Potassium carbonate–glycerol	140°C, 100 min, solid to liquid ratio (1:10, w/v)	Enhanced delignification
Switchgrass	Choline chloride–p–coumaric acid	160°C, 3 h	Glucose yield: 85.7% Xylose yield: 28.8%, Delignification: 60.8%

468

469

470

471

472   At this experimental conditions, enhancement of the hemicellulose hydrolysis process
473   occur, followed by liberation of such materials *i.e.,* promotion and transformation of the
474   degraded hemicelluloses and lignins that there obviously occur upgradation of the hydrolyzed
475   cellulose moieties into fermentable C_5 and C_6 sugar units at high temperature and pressurized
476   medium (Agbor et al., 2011; Bajpai, 2016c). Moreover, the release of AcOH (acetic acid) from
477   hydrolysis of hemicelluloses associated with acetyl groups in LCB materials takesplace, which
478   may further catalyse (autocatalysis) and enhance the hydrolysis or autohydrolysis of
479   hemicellulose moieties into fermentable glucose and xylose monomers. The optimal enzymatic
480   hydrolysis and solubilization of hemicelluloses are favourably takenplace at lower temperature
481   (at 190 ºC) and longer residence time (at 1 min) *i.e.,* the utilization of acid catalysts such as HCl,
482   HNO_3, H_2SO_4, CO_2 or SO_2, *etc.,* enhances the recovery of sugar moieties from hemicellulose and
483   thereby decrease in the production of inhibitory compounds during the consequent fermentation,
484   followed by the enzymatic hydrolysis processes (Agbor et al., 2011; Bajpai, 2016c).This
485   pretreatment process is more efficient for hardwoods as well as agricultural residues, but less
486   efficient for softwood materials. The main advantages of using SP method are (i) efficient and
487   eco–friendly process, (ii) very little quantity of chemicals utilized, (iii) requirement of low
488   energy input with low cost, *etc*. However, the main disadvantages of employing the SP approach
489   are the partial or incomplete destruction of lignin–carbohydrate matrix (LCM), which is leading
490   to a high threat of condensation. Aslo, the precipitation of soluble lignin moieties that obviously
491   cause the LCB less digestible, destruction of xylan contents in hemicelluloses and the generation
492   of fermentation inhibitors at very high temperatures. This process requires washing of the formed
493   hydrolysates, during the fermentation process that eventually may lower the overall
494   saccharification yields (20–25 %) (Agbor et al., 2011; Bajpai, 2016c).

495

496   **3.1.3. Supercritical carbon dioxide explosion (*Sc*–CO$_2$) pretreatment**

497

498   Currently, most of the scientists have been tried to upgrade the LCB pretreatment
499   processes with cheaper chemicals at optimum experimental conditions (operation at lower
500   temperature than SP treatment). in this regard the supercrititocal carbon dioxide (*Sc*–CO$_2$)
501   pretreatment process in physico–chemical approaches has shown excellent results, when
502   compared to other pretreatments (Ravindran and Jaiswal, 2016). Generally in *Sc*–CO$_2$ process,

503   the supercritical fluids are compressed at roomtemperature above its critical point (Ravindran

504   and Jaiswal, 2016), thereby the $CO_{2(g)}$ molecule is the most commonly used supercritical fluid,

505   since it is non–harmful, nonflammable, recyclable, and low–cost compound with low critical

506   temperature and pressure (31.1 °C and 73.6 bar, respectively). Furthermore, the $CO_{2(g)}$ molecules

507   are dissolved in H_2O to form carbonic acid, which causes very less corrosiveness. This Sc–CO_2

508   method is operated at very low temperature that helped to prevent the decomposition of sugar

509   moieties in the presence of acidic solvents. Normally, LCB pretreatment with Sc–CO_2 usually

510   leads to delignification of lignocellulosic materials. During the LCB pretreatment process, the

511   CO_2 molecules enter into small pores of LCB materials, due to its small size (Ravindran and

512   Jaiswal, 2016) *i.e.,* cellulosic structure is disrupted, when CO_2 pressure is released which

513   ultimately increased the accessibility of the substrate to the cellulolytic enzymes for the process

514   of hydrolysis.

515

3.1.4. Co–solvent enhanced lignocellulosic fractionation (CELF) pretreatment

517

518   In this CELF method, a mixture of tetrahydrofuran (THF) and H_2O is utilized as a

519   monophasic solvent system and this LCB pretreatment process involves the delignification

520   followed by conversion of glucose–rich LCB materials into high value–added fuels, including

521   5–HMF, FF and LA (Ashokkumar et al., 2022). CELF pretreatment technology is more

522   effectively utilized for hardwoods, raw maple wood as well as raw corn stover. In this

523   pretreatment process, an aqueous mixture of tetrahydrofuran (THF) with dilute mineral acids has

524   been applied to enhance the LC biomass deconstruction *via* upholding the extensive

525   delignification as well as solubilization of LCB with insignificant sugar degradation (Nguyen et

526   al., 2016). This CELF method generates high percentage yields of simple fermentable sugar units

527   and their dehydration products like 5–HMF, FF and LA, *etc*. The selection of Lewis base THF

528   solvent in CELF methods is because of its low boiling point (66 ºC), ease of recovery, recycling

529   as well as reutilization of solvents. Application of unique polar aprotic ether as solvent with

530   alternate to dioxane is owing to its easy coordination with both Lewis acids as well as strong

531   Bronsted acids and simply miscible or azeotrope nature with water over a wide range of

532   concentrations (Cai et al., 2013; Nguyen et al., 2016, 2015; Smith et al., 2016). Further, THF

533   may be considered as a renewable solvent, which can be derived from maleic anhydride, 1,4–

534   butanediol or furfural that are catalytically generated from C_5 sugar moieties (Meng et al., 2018).

535   During the CELF method, the presence of dilute mineral acids accelerate delignification process

536   at very low temperature and also prevent the degradation of THF. At higher temperatures (at 170

537   ^{o}C or higher), this CELF method produces high yields of fuel precursors, comprising of FF,

538   5–HMF and LA, that directly from LC biomass. Also, the polar aprotic THF is associated with

539   water and showed that it never distilled to dryness and reduced the generation of peroxide

540   formation, as it permits safe upgrading of LCB materials for industrial applications (Smith et al.,

541   2016). CELF method was applied to corn stover at moderate 1:1 (v/v) THF: water ratios, study

542   showed ~ 95 % recovery of total xylose, glucose and arabinose sugar units, using only very low

543   enzyme loadings (2 mg–protein g–glucan–in–RCS^{-1}) (Nguyen et al., 2016). About 85–95 % of

544   acid insoluble Klason lignin materials can be removed from LC biomass, during CELF

545   pretreatment that results in the precipitation of a very clean lignin product, also called CELF

546   lignin, from the liquid phase after recovery of the THF by low–temperature vacuum distillation.

547   Patri et al., studied the THF co–solvent with mineral H_2SO_4 (act as catalyst) on enzymatic

548   hydrolysis of switchgrass biomass, yielded approximately 90 % glucose at 160 ^{o}C (Patri et al.,

549   2021). The combining CELF pretreatment with simultaneous saccharification and fermentation

550   (SSF) methods showed very high yields on ethanol fermentation at high LC biomass solids

551   loadings (Cai et al., 2013; Nguyen et al., 2016, 2015).

552

4.   Future directions

554

555   Sustainable 2G lignocellulosic derived biorefineries has been expected as an alternative

556   to the raised growing energy crisis and environmental uncertainty. The lignocellulosic derived

557   biofuels can be feasibly produced *via* conventional routes. Exceptionally it is in the laboratory

558   scale level only in the aspects of certain technical as well as large–scale commercial

559   sustainability issues and is owing to the various processing steps involved in it. In this regard, it

560   is mandatory that development of innovative pretreatment technologies to facilitate the large–

561   scale productivity from lignocellulosic biorefineries (Ravindran and Jaiswal, 2016; Sankaran et

562   al., 2020). The proposed pretreatment technologies possess exclusive potentiality to get better

563   yield along with operational flexibility from 2G lignocellulosic biomasses, further it is not at all

564   energy–intensive for commercialization. The physical pretreatments effectively reduces size of

565   the components of lignocellulosic biomass materials, crystalline index of the celluloses,

566   consequently move up the accessibility for the active sites. This technique mainly includes the

567   mechanical shredding by means of milling & chipping (grinding), steam explosion, AFEX

568   (ammonia based pretreatment), some radiation–based ultrasonication, γ–electron beam and

569   microwave processes (Lu et al., 2021). The chemical pretreatment, involves degradative path of

570   components of lignocellulosic moiety in aquatic medium by certain chemical factors namely

571   acidic & alkaline hydrolysis, alkaline & metal salts, organo–solvents, ionic liquids (ILs) and

572   DES (deep eutectic solvent). The physico–chemical conversion of lignocellulosic biomass

573   components has been introduced to replace certain inconveniencies caused by the both physical

574   and chemical pretreatments towards the industrial applications. It majorly consists of extractive

575   ammonia (EA), soaking aqueous ammonia (SAA), supercritical fluids (SCF) *viz* supercritical

576   carbon dioxide (*Sc*–CO_2), supercritical water (*Sc*–H_2O): and supercritical ammonia (*Sc*–NH_3)

577   explosion, LHW [liquid hot water techniques *via* hydrothermolysis & uncatalyzed solvolysis

578   processes], SPORL (microwave assisted chemcial and sulfite pretreatment) pretreatment,

579   hydrothermal (HT) explosion and wet air oxidation to surmount the recalcitrance nature of the

580   lignocelluloses (Moodley et al., 2020). In the case of various green bio–pretreatment pathways,

581   which predominantly incorporate certain microorganisms *via* bacterial and fungal species for

582   degradation of hemicelluloses as well as lignin components, by means of enhanced selective

583   enzymatic saccharification improve both the hemicelluloses and lignins solubility to

584   destructuralize the lignocellulose components for the enhancement in the accessiblity to specific

585   enzymes with slight environmental crash (Sankaran et al., 2020). The bio–conversion into

586   bioenergy and high value added by–products during the different pretreatment techniques, which

587   have been utilized in large industrial scale, till possesses considerable challenges like energy

588   requirement, low efficiency, formation of hazardous wastes to inhibit the yield of fermentable

589   sugars, partial degradation of cellulose and lignocelluloses *etc*. Thereby, a need of an emerging

590   environmental friendly technique that compensates all the above mentioned challenges like

591   necessitation of green solvents, low chemicals & energy consumption, usage in minimization of

592   water, flexible operation with tiny particles, *etc* (Sankaran et al., 2020). A combined microwave–

593   chemical (–acid and –alkali) pretreatment was employed to replace conventional acidic/alkaline

594   pretreatment and it proves that the combined treatments enhance the yield of fermentable sugars

595   quickly (Diaz et al., 2013; Singh et al., 2022). Another study recommended low–energy

596   ultrasonic—chemical (–alkali) pretreatment to enhance the lignocellulosic biodegradability. The

597   Ionic liquid–ultrasound combination process with bagasse is biocompatible for cholinium IL, and

598   it results in 80 and 72% of the celluloses and hemicelluloses saccharification process along by

599   way of a modest inhibitory consequence on the activity of enzyme celluloses (Baruah et al.,

600   2018). The commercial production of bio–ethanol was achieved by three pretreatment techniques

601   viz. dil. acids, liquid hot water and AFEX. Though, in the view of techno–economical analysis,

602   the LHW pretreatment can be considered as a commercial one (Zhao et al., 2013).

603

604   **5.   Critical knowledge gaps and research needs**

605

606   It is challenging that ease of large–scale conversion of lignocellulosic biomass into

607   fermentable sugars *via* ifferent pretreatment stages is neither cost–effective nor competitive

608   technology. Since the existence of lignin in the biomass materials inhibits the hydrolytic process

609   of both celluloses and hemicelluloses (Baruah et al., 2018). Accordingly, wide research

610   knowledge is required to develop different biomass pretreatment processes to delignify it. The

611   current well–known pretreatment processes are commonly energy–intensive, in that way

612   resourceful and cost–effective pretreatment techniques is given preference for implication in the

613   industrial point of view (Lu et al., 2021). Recently the research reveals that acids and bases

614   chemical pretreatment/bioconversion techniques to treat the lignocellulosic biomass feed are

615   predictably cost–effective and commercially viable, since purified form of the by–products can

616   obviously be reutilized as value–added products mainly drugs like compounds and optimized

617   production of bio–ethanol (Banoth et al., 2017; Nahak et al., 2022; Sewsynker–Sukai et al.,

618   2020). On the other hand, research gaps in knowledge on critical analyses of pretreatments can

619   be rectified to conclude that whether the pretreatment technique is a tailor–made process to each

620   biomass material individually and chosing particular biomasses, based on their characteristics for

621   the best generation of bio–fuels. Also, it must be optimized to provide a single pretreatment

622   process to perform an absolute delignification process to biomass in commercial as well as eco–

623   friendly point of view. Further, to gain the pretreatments by dil. acidic hydrolysis in the case of

624   scaling–up of bio–fuels production through conversion of hemicelluloses into soluble sugars is a

625   highly efficient process and it entirely depends on various operational parameters like acid

626   dosage, pressure, retention time, molar ratio of solid/liquid, reaction temperature, *etc.,* should be

gathered (Sankaran et al., 2020). Simultaneously, the knowledge to provide production of certain inhibitors like furfural and phenolics, *etc*., prevention of these toxic compounds can be performed by means of choice of lignocellulosic biomasss material and a simple strategy that would be lying on the fact that cautious application of mild pretreatments. In the case of enzymatic pretreatment, the complete removal of toxic compounds can be performed by employment of certain enzymes like laccase, peroxidases, *etc*. The combined structure of pretreatment techniques and enzymatic hydrolysis are often more effective performances and such techniques majorly depend on choice, while handling the biomasses kinds (Ravindran and Jaiswal, 2016). Consequently, this lignin components have been consumed for the commercial production of high–value added materials by means of direct combustion to provide adequate energy for industrial purposes. In this view, fast pyrolytic procedure is currently becoming accustomed by the interest of researchers as it possesses the potentiality to the effective conversion of lignin to high commercially value added products like bio–char, bio–oil, *etc*. But the production of gaseous phase bio–fuels for the industrial purpose, a well defined particular approach is necessary to comprehensively analyze the overall operation cost. In such a way that the the research knowledge provides ease of production of bio–H and some other bio–fuels from lignocellulosic biomass materials is simple *via* these processes by producing simple bio–molecules (Sankaran et al., 2020). Furthermore, the ease of production of biogas *via* anaerobic digestion, frequently is one of the heat generating integrated processes. . Additionally, the research knowledge on such techniques proffer high–digestible biomass feed apart from the fact that recycling, recovery and consumption of so produced solids and liquids from the wastewater souces

6.   Conclusions

This critical review comprises of greener pretreatment approaches *viz*. green solvent–based ILs and DES, steam expolsion, *Sc*–CO_2 and CELF pretreatments for various lignocellulosic biomass materials. Further, the steam explosion can be considered as a core technology for agricultural residues–derived bio–fuel production in industrial scale since it was revealed that corn–stover yields 80 and > 90 % of hemicelluloses and celluloses, respectively in a 50 m^3 industrial reactor *via* consequent hydrolysis. It can be suggested that the

658 combined/hybrid pretreatment methods are successful to carry out various biomass pre–
659 processing to develop a combined pretreatment technique with probability.
660

661 **CRediT authorship contribution statement**
662

663   Jeyaprakash Dharmaraja Conceptualization, Writing – original draft, review & editing.
664 Sutha Shobana: Conceptualization, Writing – original draft, review & editing, Sundaram
665 Arvindnarayan: Writing – review & editing. Rusal Raj Francis: Writing – review & editing
666 Rajesh banu: Writing – review & editing, Rijuta Saratale: Writing – review & editing, Shashi
667 Bhatia: Writing – review & editing, Ashok Kumar Veeramuthu: Writing – review & editing,
668 Vinod Kumar: Writing – review & editing, Gopalakrishnan Kumar: Writing – review & editing,
669 Funding acquisition, Project administration & Supervision.
670

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672

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981   **Highlights**

982   • Structural composition of lignocellulose biomass was provided.

983   • Advanced green pretreatments on effective destruction of biomass have been discussed.

984   • Novel green solvent–based IL and DES pretreatment are discussed.

985   • Mechanistic path of greener ionic liquid pretreatment process has been deliberated.

986   • Supercritical carbon dioxide explosion (Sc–CO_2) has been documented.

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