

Journal Pre-proofs

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

Jeyaprakash Dharmaraja, Sutha Shobana, Sundaram Arvindnarayan, Rusal Raj Francis, Rajesh Banu Jeyakumar, Rijuta Saratale, Ashok Kumar Veeramuthu, Shashi Kant Bhatia, Vinod Kumar, Gopalakrishnan Kumar

PII: S0960-8524(22)01661-3

DOI: <https://doi.org/10.1016/j.biortech.2022.128328>

Reference: BITE 128328

To appear in: *Bioresource Technology*

Received Date: 2 October 2022

Revised Date: 8 November 2022

Accepted Date: 11 November 2022



Please cite this article as: Dharmaraja, J., Shobana, S., Arvindnarayan, S., Francis, R.R., Jeyakumar, R.B., Saratale, R., Veeramuthu, A.K., Bhatia, S.K., Kumar, V., Kumar, G., Lignocellulosic biomass conversion *via* greener pretreatment methods towards biorefinery applications, *Bioresource Technology* (2022), doi: <https://doi.org/10.1016/j.biortech.2022.128328>

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

Lignocellulosic Biomass Conversion via Greener Pretreatment Methods towards biorefinery applications

Jeyaprakash Dharmaraja ¹, Sutha Shobana ², Sundaram Arvindnarayan ³, Rusal Raj Francis ⁴,
Rajesh Banu Jeyakumar ⁵, Rijuta Saratale ⁶, Ashok Kumar Veeramuthu ⁷, Shashi Kant Bhatia ⁸,
Vinod Kumar ⁹, Gopalakrishnan Kumar ^{10, 11, *}

¹Division of Chemistry, Faculty of Science and Humanities, AAA College of Engineering and Technology, Amathur–
626005, Virudhunagar District, Tamil Nadu, India.

²Green Technology and Sustainable Development in Construction Research Group, School of Engineering and
Technology, Van Lang University, Ho Chi Minh City, Vietnam.

³Department of Mechanical Engineering, Lord Jegannath College of Engineering and Technology, Marungoor –
629402, Kanyakumari District, Tamil Nadu, India.

⁴Department of Chemistry, Birla Institute of Technology & Science, Dubai International Academic City, Dubai
Campus, Box 345055, Pilani, Dubai.

⁵ Department of Life Sciences, Central University of Tamil Nadu, Neelakudy, Thiruvavur–610005, Tamil Nadu,
India

⁶Department of Food Science and Biotechnology, Dongguk University–Seoul, Ilsandong–gu, Goyang–si,
Gyeonggi-do, 10326, Republic of Korea

⁷Center for Transdisciplinary Research, Department of Pharmacology, SDC, Saveetha Institute of Medical and
Technical Sciences, Saveetha University, Chennai 600077, India.

⁸Department of Biological Engineering, College of Engineering, Konkuk University, Seoul 05029, Republic of
Korea

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

¹⁰School of Civil and Environmental Engineering, Yonsei University, Seoul 03722, republic of Korea

¹¹Institute of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University
of Stavanger, Box 8600 Forus 4036, Stavanger, Norway

***Corresponding Author:**

Gopalakrishnan Kumar, Email: gopalakrishnanchml@gmail.com

Abstract

Lignocellulose biomass during pretreatment release various compounds, 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 explosion, 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-CO₂; CELf.*

1. Introduction

Recently, there is a rapid depletion in petrochemical or fossil fuel products that leads to drastic variation of the universal economic, environmental and public 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

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

The effective and economically feasible LCB pretreatment methods mainly depend on (i) less energy-intensivity, (ii) cost-effectivity, (iii) reduction in the cellulose crystallinity, (iv) decrease in the LCB particle size, (v) excellent surface area of enhanced enzymatic hydrolytic process, (vi) utilization of low cost and eco-friendly chemicals or solvents, (vii) formation of no enzyme/toxic compounds or corrosive inhibitors, and (viii) delignification of the LCB materials without modification of native lignin structure (Anu et al., 2020; Ashokkumar et al., 2022; Mankar et al., 2021; Rasool et al., 2021). The physical pretreatment processes that include concentrated or mild inorganic mineral acids (H₂SO₄, HCl, HNO₃, etc) and organic acids (say acetic acid, oxalic acid, fumaric acid, maleic acid, etc) are effectively transfigure and detachment of the LCB materials into simple C5 (pentoses) and C6 (hexoses) units. Some of the key factors like crystallinity of celluloses, biomass porosity, active surface areas, rate of hydrolysis, degree of acetylation & polymerization, etc., are delineating the pretreatment processes industrial and energy oriented as well as making eco-friendly feasibility (Anu et al., 2020; Ashokkumar et al., 2022; Rasool et al., 2021). Hence, this present review provides a detailed information on the recently developed greener approaches *viz* ionic liquids (ILs), deep eutectic solvents (DESs),

steam explosion (SE) or steram pretreatment (SP), Supercritical carbon dioxide ($Sc\text{-CO}_2$) and co-solvent enhanced lignocellulosic fractionation (CELFF) pretreatments. A widespread description on development of the accessible pretreatment methods are also covered and this review will help the readers getting an unambiguous details on the recent advances in the greener pretreatment methods and also inspire them working on novel pathways for upgrading of a LCB-based refinery in the near future.

2. Lignocellulosic materials

Based on the resource of LCB materials, the specific structural compositions of lignocellulosic content could be varied. Table 1 summarizes the various LCB material sources with their structural compositions. Most of the LCB materials are comprised of polysaccharides, which are altered into simple monosaccharides or sugar units *via* numerous fermentation processes (Bajpai, 2016a). In general, the fermentable sugar compositions of celluloses, hemicelluloses and lignins are mainly depending on the nature of LCB biomass materials. The rigid cell wall structure of the plants is comprised of cellulose, which is overcovered by lignin and hemicellulose moieties. Table 1 clearly has shown that the high percentage of cellulose and hemicellulose contents are predominantly present in LCB materials. The ~ 30–50 % of celluloses $[(C_6H_{10}O_5)_n]$ are the primary as well as significant key chemical components of LCB materials. The primary cell wall of cellulose structure is mainly comprised of very stable linear amphiphilic homopolysaccharide polymers of β -D-glucopyranose moieties in the range of 10,000–15,000 D-glucose or cellobiose (monomeric) units, which are linked *via* (β -1–4)-glycosidic bonds to form more microcrystallinity (50–90 %) with less amorphous (10–45 %) structural nature (Agbor et al., 2011; Bajpai, 2016a; Bhatia et al., 2020; Lorenci Woiciechowski et al., 2020; Mankar et al., 2021). The linear long chain amphiphilic homopolysaccharide polymers of celluloses are staked as multiple overlapping layers to the axial position of –OH groups. The air stable polymeric long cellulose chains of cell wall structure are formed by inter- and intra-molecular hydrogen bonds and van der Waals forces of attraction *i.e.*, approximately 20–300 cellulose chains are clustered to create microfibrils with an hydrophobic interior as well as hydrophilic exterior structure and the bundle of microfibrils generate cellulose fibres (Agbor et al., 2011; Bajpai, 2016a).

Table 1. Compositions of various sources of LCB materials.

LCB material sources	Major chemical compositions			Refs.
	Cellulose (%)	Hemicellulose (%)	Lignin (%)	
Grasses and Weeds (Herbaceous crops)				(Dharmaraja et al., 2019; Mankar et al., 2021; Moodley et al., 2020; Sankaran et al., 2020)
Amur silver-grass	42.00	30.15	7.00	
Bamboo	41.80	18.00	29.30	
	46.50	18.80	25.70	
	26–43	30.00	21–31	
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	
<i>C. odorata</i> (Siam weed)	41.00	17.30	20.70	
Elephant grass	47.12	36.01	11.50	
<i>Eichhornia crassipes</i>	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	
<i>Lantana camara</i>	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	
<i>Saccharum spontaneum</i>	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., 2022; Dharmaraja et al., 2019; Hassan et al., 2018; Kumar et al., 2020, 2019)
Acacia pruning	49.00	13.00	32.00	
American sycamore	37.20–41.80	17.60–19.60	25.00–27.30	
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	
<i>Pinus armandii</i> 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.,
<i>Gmelina arborea</i> sawdust	23.00	–	23.30	2022; Ummalyma et
<i>Salvadora oleoides</i> 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 microfibrils and these microfibrils 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

% of the total biomass sources. It is comprised of highly amorphous, branched short side chains, and heteropolysaccharide polymeric nature with C₅ (β -D-xylose & α -L-arabinose) and C₆ (D-glucose, D-mannose & D-galactose) sugar units, sugar acids (α -D-4-O-methyl-D-glucuronic, α -D-galacturonic and α -D-glucuronic) and a tracer amount of α -L-fucose, L-rhamnose, acetyl groups and uronic acids (Bajpai, 2018, 2016a; Bhatia et al., 2020; Lorenci Woiciechowski et al., 2020; Mankar et al., 2021; Yousuf et al., 2019). The backbone of hemicellulose structure is fashioned through heteropolysaccharide polymer chains of C₅ and C₆ monomeric sugar units with short lateral branches. The sugar units are linked through β -1,4-D-glucosidic bonds, which all through make the outer surface of the cellulose is more rigidity and provide more amorphous matrix as well. The lignin [(C₁₀H₁₁O_{3.5}); of ~ 10–20 % the total LCB sources is the third most rich organic heteropolymeric compound after the cellulose and it is liable for high hydrophobic as well as rigidity in structural nature. It binds cellulose to hemicellulose in the plant cell wall like sandwich bind, it also confers a rigid, impermeable, resistance to any microbial attack as well as oxidative stress. Lignin is a very complicated 3D amorphous complex with polyphenol structural feature, due to high molecular weight and degree of cross-linked polymers of phenylpropane monomeric units (Brandt et al., 2013; Hosseini Koupaie et al., 2019; Zoghلامي and Paës, 2019). The biopolymeric structure of lignin moiety contains a cross-linked phenylpropanoid units and has widely been utilized as the key chemical precursors as well as alternative to low-cost renewable feedstock materials. Generally, the lignin is an amorphous heteropolymeric network with hydroxylated and methoxylated phenylpropanoid monomeric or monolignol units namely, *p*-coumaryl alcohol or *para*-hydroxyphenyl (H-unit), coniferyl alcohol or guaiacyl (G-unit) and sinapyl alcohol or syringyl (S-unit) (Nimmanterdwong et al., 2021; Yousuf et al., 2019; Zoghلامي and Paës, 2019). Furthermore, the relative amount of H/G/S-units present in the various biomass plant materials are 5, 95 and 0 % for softwoods (pinus and spruce), 0–8, 25–50 and 45–75 % for hardwoods (birch, beech and aspen) and 5–35, 35–80 and 20–55 % for grasses, respectively (Li et al., 2016). The existence of the above interlinked ether (C–O–C) and C–C bond linkages such as β -O-4, α -O-4, β -5, 5-5, β -1 and β - β of lignin provide a highly heterogeneous nature with 3D complex polymeric structure. This linkages have been catalyzed to produce variety of high value added aromatic by-products such as ethylbenzene, guaiacol, *p*-hydroxyl acetophenone, *etc.*, (Garedew et al., 2021). Furthermore, lignin showed physically very limited polysaccharide accessibility and also binds the different

components of LCB together, thus making it as insoluble water components. Also, it plays a role as physical barrier that blocks the access of enzymes to cellulose *i.e.*, lignin acts as key obstacle to enzymatic and microbial hydrolysis of LCB materials.

3. Various LCB pretreatment methods

In general, the effectiveness of LCB pretreatments accomplished by economic and environmental feasibilities *i.e.*, to employ an efficient LCB pretreatment technology should be attentive in view of their cost-reduction, environmental concerns, and sustainability, that leads to increase the specific surface area and porosity, cellulose digestibility by disrupting the rigid carbohydrate-lignin matrix, reduction of the particle size, removal of hemicellulose/lignin content, *etc.*, which resulting an high percentage of simple sugar unit recovery after enzymatic hydrolysis (Ashokkumar et al., 2022; Raj et al., 2022). Hence, the breakdown of hemicelluloses as well as lignin contents present in the plant cell walls through various pretreatment technologies, before the enzymatic digestion process leads to enhance the generation of simple fermentable sugar units into biofuels and biocompounds production from LCB materials (Shirkavand et al., 2016). The effective LCB pretreatment process should possess (i) formation of high percentage of fermentable sugar unit contents during downstream processing, (ii) pretreatment tools applied for all types of LCB materials, (iii) recovery of lignin and hemicellulose moieties for consequent combustion process, (iv) minimum or low generation of co-products or inhibitors for subsequent pretreatment process, (v) efficient recovery of lignin content for further conversion or production into high value added biocompounds, (vi) avoiding the degradation of pentoses derived from hemicellulose moieties, (vii) minimization of the cost effective pretreatment process by applying eco-friendly chemicals or solvents, moderate size of reactors as well as minimizing the energy consumption (both heat and power) routes, *etc.*, (Cheah et al., 2020; Shirkavand et al., 2016). Recently, the most advanced LCB pretreatment technologies are typically categorized into four methods namely physical, chemical, physico-chemical, and biological (Ashokkumar et al., 2022; Ummalyma et al., 2019). The key objective of physical pretreatment includes the utilization of mechanical operations including grinding, ball milling, screw pressing, soaking or pelleting, mechanical extrusion, freezing, microwave, ultrasonication *etc.*, which reduce the crystallinity and particle size of LCB materials, that leads

to increase the surface area and degree of polymerization (DP) of LCB into fast digestion as well as solubilization (Hendriks and Zeeman, 2009; Shirkavand et al., 2016; Yadav et al., 2020). In addition, there is no formation of toxic materials or inhibitors, it is the chief feature of these technologies (Shirkavand et al., 2016). The mechanical grinding operations mainly reduce the particle size, DP and crystallinity of LCB, which further increased the rate of enzymatic hydrolysis process and the generation of biofuels and biocompounds (Chandel et al., 2022). The pelleting or soaking methods, utilization of mineral acid/base or alkaline solution improves the enzymatic LCB digestibility to reduce the cellulose crystallinity and also upgrades the delignification rate. By applying ball as well as wet disk milling operations to LCB materials, there is generation of high yield on celluloses and xylose compounds after the successful enzymatic hydrolysis but such operations consume very high energy (Shirkavand et al., 2016). During the mechanical extrusion operation to LCB materials, face shearing, mixing as well as heating, lead to a sudden reduction of particle size in DP of LCB. However, using the microwave or ultrasound or pulsed electric field process, the LCB materials are treated with high energy EMR (electromagnetic radiation or wave) for a short time period, it degrades the cellulose and hemicellulose fraction structure *i.e.*, such kind of operation more effectually removes hemicellulose and lignin moieties present in LCB and also it interrupts the ester and ether linkages present in both cellulose and lignin moieties. Then only it can readily undergo hydrolysis process with generation of high yield efficiency for simple fermentable sugar units, but such methods are cost-intensive (Chandel et al., 2022; Shirkavand et al., 2016; Singh et al., 2022; Yadav et al., 2020). The cavitation effect on principle of ultrasound radiation technology is widely being applied on LCB pretreatment process that leads to breakdown the lignin α -O-4 and β -O-4 linkages. Recently, a novel freezing and thawing approaches are widely being utilized in physical pretreatment process of LCB materials (Singh et al., 2022). But, one major drawback for utilization of the physical pretreatment is the energy consumption (Tu and Hallett, 2019). Further, this physical technology is not suitable for large-scale industrial process, due to its high energy requirements. The chemical pretreatment methods, including acid hydrolysis (mild & concentrated mineral HCl, H₂SO₄, HNO₃, *etc.*, and organic oxalic, maleic, succinic acids, *etc.*), alkaline or base hydrolysis (KOH, NaOH, Na₂CO₃, CaO, CaCO₃/Ca(OH)₂, NH₃, *etc.*), organic solvents and greener ionic liquid as well as deep eutectic solvent methods are broadly employed to breakdown directly the cellulose and hemicellulose fractions in LCB

materials and hydrolyses the bonds that leads to generate the monomeric C₅ and C₆ sugar units, which are converted into high value added biocompounds and biofuels (Bhatia et al., 2020; Kant Bhatia et al., 2022; Solarte–Toro et al., 2019; Tian et al., 2018).

Generally, acid pretreatments are extensively employed for LCB pretreatment technologies, due to its low cost and high efficiency to hydrolyse the hemicellulose contents into monomeric fermentable sugar units without dissolving lignin moieties. But, the major drawback for this hydrolysis method is the formation of high value added lignin by-products like furfurals (FF), 5-hydroxymethylfurfural (5-HMF) and phenolic acids, which are more corrosive as well as microbially toxic intermediate inhibitor compounds, high acidic wastewater generation, *etc.*, thereby, need to recovery as well as neutralization of acids (Kant Bhatia et al., 2022). While applying this method to LCB materials, the common disadvantages are extremely effective at deconstruction, the production of toxic or inhibitor compounds, carbohydrate loss and high cost (Anu et al., 2020; Shirkavand et al., 2016).

In addition, the combined physical and chemical pretreatments in physico-chemical technologies such as ammonia-based (AFEX : Ammonia fiber/freezing explosion, ARP : Ammonia recycle percolation, and SAA : Soaking aqueous ammonia), supercritical fluids (SCF) explosion, wet oxidation, steam explosion and liquid hot water (LHW) pretreatments are effectively utilized on different types of LCB materials towards the production of fermentable simple sugar contents. Also the deconstruction of LCBs, using such technologies is more predictable with immediate discharge of high pressure that leads to breaking down of the complex network structure of LCB materials within a short period of time. Further, the biological pretreatment techniques are generally more superior than other pretreatment process (Anu et al., 2020; Dey et al., 2022; Hassan et al., 2018; Yadav et al., 2020) because these kind of methods offer various advantages such as low capital cost & energy, decrease in the dependence on chemicals, minimum formation of inhibitors. But the main disadvantages are the low hydrolytic rate and requirement of very long pretreatment times. This pretreatment mainly involves the utilization of microbes such as white rot, brown rot and soft-rot fungus or metabolites from enzymes such as peroxidase, hydrolases, ligases, laccases, oxidoreductase, isomerases, *etc.*, are mostly utilized in these pretreatment processes due to their special lignolytic and delignification

properties. They are playing a vital role to degrade hemicellulose and lignin contents and also depolymerization of LCB, outside plant cell wall *i.e.*, delignification and saccharification of LCB components, before the enzymatic hydrolysis (Anu et al., 2020; Dey et al., 2022; Hassan et al., 2018; Yadav et al., 2020). Moreover, the effective LCB pretreatments are also affected by various issues of physical and chemical properties such as cellulose crystallinity, lignin content, the existing linkages between cellulose and lignin (Ashokkumar et al., 2022; Ummalyma et al., 2019). Hence, a simple or particular LCB pretreatment technology does not provide an efficient and expected LCB degradability results. So, the combined pretreatment processes, which are integrating two or more pretreatment technologies from the above mentioned four methods showed more effective and upgraded LCB pretreatment than application of single process (Ummalyma et al., 2019).

3.1. Greener pretreatment approaches

Currently, the concept of 12 principles of green chemistry or greener concepts have widely been studied and also utilized as an emerging pretreatment process to the challenge of upgrading any type of LCB materials feasibly to biorefinery approach into valuable compounds. Various LCB pretreatment technologies are already available, but some of them are greenest as well as economical technologies mainly like Ionic liquids (ILs), Deep eutectic solvents (DESs), steam explosion (SE) or steam pretreatment (SP), supercritical carbon dioxide explosion (*Sc*-CO₂), Co-solvent enhanced lignocellulosic fractionation (CELf), *etc.*, are well proven that the formation of low or no inhibitors, enhanced conversion rate of complex polysaccharides into fermentable simple sugar units generation and other value added biofuels and biocompounds formation from LCB materials in large scale industrial processes (Hassan et al., 2018; Sharma et al., 2022; Usmani et al., 2020). Recently, the state-of-art in the development of novel greener technologies showed chief promising as well as convincing methods in the field of LCB pretreatments. The selected greener approaches are currently being employed for LCB pretreatment methods and are summarised in Table 2.

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 Crushing, Shredding)	(Ball & Hammer Cutting, Shredding)	Reduce the particle size and disrupt the crystallinity	Control of final particle size, easy handling, less water consumption, free from chemical intake, increased surface area, low production cost	High energy consumption than inherent biomass energy, low release of sugar content, commercial feasibility is very less, inability to remove lignin which restricts the access of the enzymes to cellulose and inhibit cellulases
Irradiation (Microwave Ultrasound)	and	Swelling and fragmentation of lignocellulosic material	Fast heat transfer, short reaction time, energy efficient, cheap and generate less / no pollution, increased porosity, highly efficient at batch scale, dissolve extractives with heating	Low penetration of radiation in bulk products, distribution of microwave power around of LCB due to non-homogeneous material, high energy consumption than inherent biomass energy, low release of sugar content, commercial feasibility is very less
Chemical pretreatment				
Acid hydrolysis (using dilute or concentrated 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	Concentrated 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 hydrolysis	Alkaline	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

		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)	Cellulose precipitation, effective depolymerizes lignin by cleavage of β -O-4 linkage, hemicellulose fractionation and lignin removal	Green solvent, biodegradable and biocompatible, working under mild reaction conditions, 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 higher pretreatment 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 size reduction	energy input with no recycling or environmental cost	decreases the overall saccharification yields, release inhibitory by-products, much less effective for softwood
Liquid (LHW)	hot water	Partial hydrolysis of hemicellulose, lignin removal	Does not require washing, chemical recovery, or detoxification 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 and energy 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 cellulose degradation	Selective degradation of lignin, hemicellulose, and cellulose, low energy required, chemical-free method, complete degradation of lignin, environmentally friendly	Long pretreatment time, low sugar release, hydrolysis rate is low

3.1.1. Novel green solvent-based ILs and DES pretreatments

Ionic liquids (ILs) or designer solvents are an alternate potent green molten salts, which are formed by the combination of bulky H-donating 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-chemical 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; Halder 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 effectually 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 microfibrils 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; Halder 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-

Butyl-3-methylimidazolium iodide, [Bmim]MeSO₄: 1-Butyl-3-methylimidazolium methylsulfate, [BmPy]Cl: 1-Butyl-3-methylpyridinium chloride, [C₄C₁im][MeSO₄]: 1,3-dimethylimidazolium methyl sulfate, [C₄C₁im][HSO₄]: 1-butyl-3-methylimidazolium hydrogensulfate, [C₄Him][HSO₄]: 1-butylimidazolium hydrogen sulfate, [C₄C₁im]Cl: 1-butyl-3-methylimidazolium chloride, [C₄C₁im][MeCO₂]: 1-Butyl-3-methylimidazolium acetate, [Emim]OAc: 1-Ethyl-3-methylimidazolium acetate, [Emim]Cl: 1-Ethyl-3-methylimidazolium chloride, [Hmim]CF₃SO₃: 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate, [Mmim]MeSO₄: 1,3-Dimethylimidazolium methylsulfate, [MBPcl]: 3-methyl-N-butylpyridinium chloride, [NMMO]: N-methylmorpholine-N-oxide monohydrate, [N4444]OAc: Tetrabutylammonium acetate, [Py]OAc: Pyridinium acetate, [Py]For: Pyridinium formate, [Py]Pro: Pyridinium propionate *etc.*, have widely been utilized for LCB pretreatment methods (Amini et al., 2021; Haldar and Purkait, 2021; New et al., 2022).

Table 3 summarizes the solubilization yield (wt %) of cellulose and lignin moieties of various LCB materials using ILs pretreatment. A mixture of ILs like [C₄C₁im][MeSO₄], [C₄C₁im][HSO₄], [C₄Him][HSO₄], [C₄C₁im]Cl, [C₄C₁im][MeCO₂], *etc.*, combined with water are effectively utilized by LCB pretreatment of various biomasses, including mainly *miscanthus*, pine, willow, maple wood, switchgrass, and oak. Moreover, the ILs can be recovered and reused after each cyclic pretreatment through different methods such as reverse osmosis (RO) and ion exchange or salting out processes (Usmani et al., 2020). After the LCB pretreatment by ILs, the separation of the liquid as well as solid parts are associated with some loss of LCB sugars, so a combination of saccharification, deconstruction and then enzymatic fermentation processes are probably required to reach the ultimate way for reducing the cost of IL operation. Brandt *et al.*, studied the pretreatment of *Miscanthus giganteus*, pine (*Pinus sylvestris*), and willow (*Salix viminalis*) biomasses with two ILs namely 1-butyl-3-methylimidazolium hydrogen sulfate [Bmim][HSO₄]⁻ and 1-butyl-3-methylimidazolium methyl sulfate [Bmim][CH₃SO₄] (Brandt et al., 2011). It showed that >90% recovery of glucose yields due to the presence of certain anions, which are the predominant sources in lignin dissolution with high recovery of cellulose moieties for LCB materials.

388

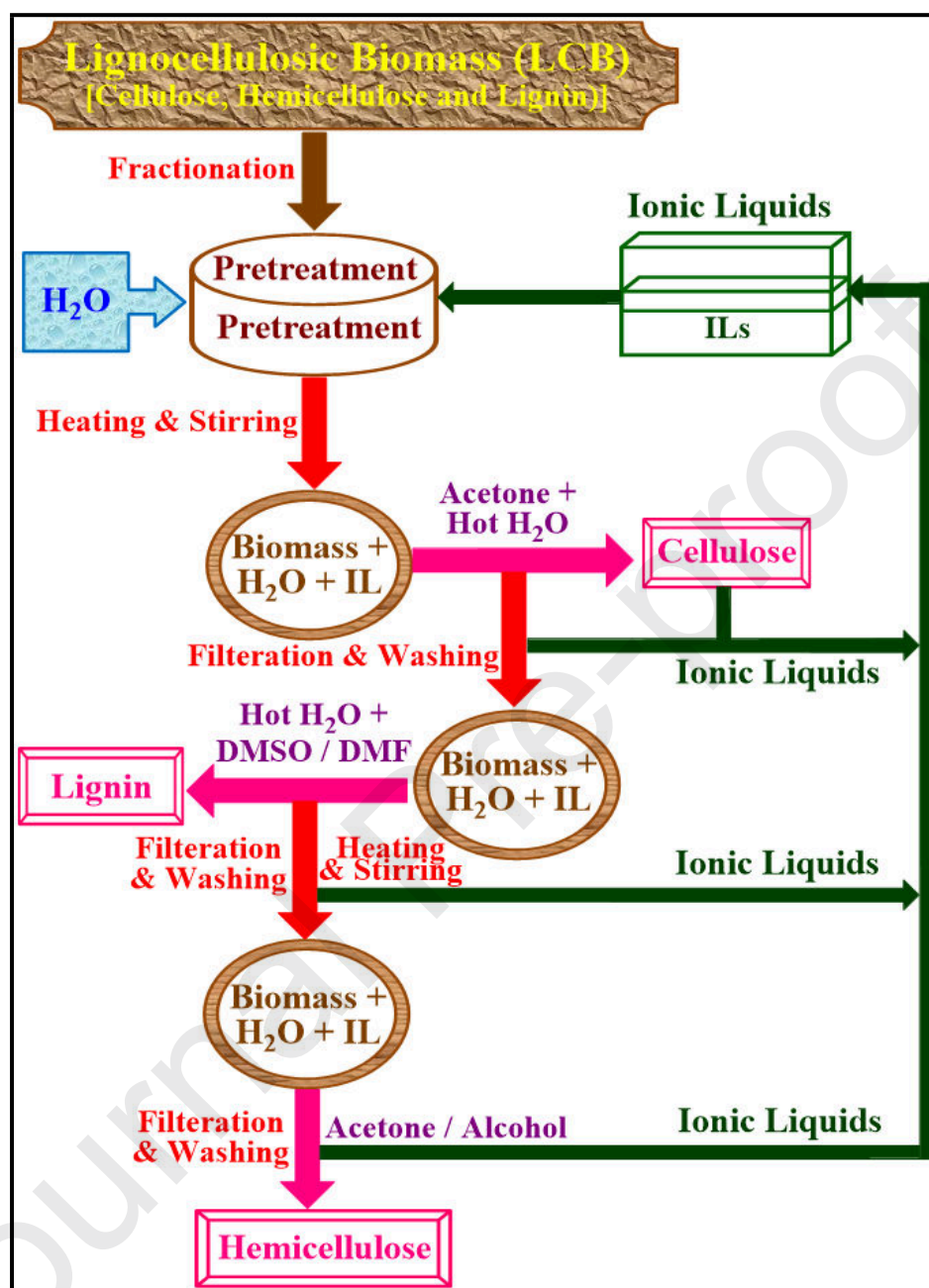


Fig. 1. LCB pretreatment process with ILs [Adopted and modified Ref. (Usmani et al., 2020)].

Table 3. Various LCB material sources under ILs pretreatment 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. (°C)	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][HSO ₄]	Convection	1 g / 10 g	8 h	120	5.00
Pine Pulp (Indulin)	[Ch][OAc]	–	5 mg / g	3 h	90	28.00

	[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 Glycol/H ₂ O]–	Stainless Steel Reactor	1 g / 30 ml	30 min	90		24.06 ± 2.65
	[Bmim][HSO ₄]						
Poplar	[1,4–Butylene Glycol/H ₂ O]–	Stainless Steel Reactor	1 g / 30 ml	30 min	90		11.12 ± 3.34
	[Bmim][HSO ₄]						
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][PF₆]: 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.

Agnieszka *et al.*, investigated the fractionation of *Miscanthus x giganteus* grass material with low-cost and economically viable IL namely [TEA][HSO₄]: triethylammonium hydrogen sulfate at a mild temperature (120 °C) (Agnieszka *et al.*, 2017). It showed an enhanced solubilization of lignin (85 %) and hemicellulose (100 %) moieties, which are on further subsequent enzymatic saccharification of regenerated cellulose yielded, 77 % of glucose units. The techno-economic analysis suggested that the cost of ILs-derived LC biomass is about 13.71 \$/kg (Bhatia *et al.*, 2020). Furthermore, the main disadvantages of using ILs on LCB pretreatment processes are (i) more viscous nature of ILs, (ii) most of the ILs are toxic for cellulase i.e., negative effect on cellulase activity, (iii) high cost of imidazolium based ILs, (iv) conventional recovery and purification process of ILs are so expensive. These are the key considerations for the large scale industrial applications. Hence, the enhanced production of simple sugar units from LCB materials assisted with ILs in an pilot-scale plant is still now needed some optimization (Bhatia *et al.*, 2020; Tian *et al.*, 2018; Usmani *et al.*, 2020).

Currently, the emerging of deep eutectic solvents (DESs) as a new generation of mild and sustainable greener solvents for LCB pretreatment process has been introduced as promising as alternatives to ILs for LCB pretreatment (Ahmed *et al.*, 2022). Since they are not only sharing most of the merits of traditional ILs, but also overcome many of their drawbacks (Sharma *et al.*, 2022). They are composed of two or three ionic compounds, which are capable of self-association to form a eutectic mixture. Also, the major milestone advantages of using DESs in LCB pretreatment process is its extensive physico-chemical properties, which are much similar to ILs (Mankar *et al.*, 2021). DESs are liquid compounds, consisting of two or more solid organic mixture of HBA (Hydrogen bond acceptor) like quaternary ammonium halide salt, metal halides, *etc.* with HBD compounds (Hydrogen bond donor) like amino acids, amines, carboxylic acids, carbohydrates, urea, *etc.* (Ahmed *et al.*, 2022; Lugani *et al.*, 2020). The most widely applied DESs are choline chloride [(ChCl)] with some urea, glycerol, carboxylic acids and polyols. They have widely been utilized in numerous fields like pharmaceuticals, bio-refineris, food productions, *etc.* Also, DESs are more emphasized in large scale industrial pretreatment as it is an economical as well as eco-friendly solvent for LCB pretreatment technique and also DESs are 20 % much cheaper than traditional ILs (Zhang *et al.*, 2021). DES solvents are promising alternatives to ILs due to their non-toxicity, low cost, environmentally friendly nature, low

volatility, wide liquid range, biodegradability, enzyme compatibility, *etc.*, (Lugani et al., 2020). Moreover, they have shown as an effective bioconversion of LCB on bench-scale experimental level. The recycling and reusability of DESs can also be increased its economic as well as technical efficiencies for LCB pretreatment technology. The HBDs are having strong electron-withdrawing groups that showing an effective as well as enhanced LCB pretreatment performance, while HBD contains $-OH$ or $-NH_2$ group that shows low or negative efficiency results. Further, the strong acidic DESs are effectively removing xylan from LCB structure. As a result, the cellulose content is available readily for enzymatic hydrolysis process, even while the presence of lignin in LCB structure (Jędrzejczyk et al., 2019). DESs pretreatment on various LCB bioconversions with their effects are summarized in Table 4. Generally, the applications of DESs on LCB pretreatment showed more effective solubilization of lignin moieties than hemicellulose and cellulose contents (Mankar et al., 2021). The presence of $-OH$ groups in DESs leads to generate strong H-bonding network with cellulose and also stabilizing the DES-Cellulose system. Procentese et al., reported that the pretreatment of agro-wastes mainly such as apple residues, potato peels, coffee silverskin, and brewer's spent grains with two DESs namely choline chloride-glycerol and choline chloride-ethyleneglycol showed the high efficiency of fermentable sugar production as compared to other pretreatments as well as ILs process (Procentese et al., 2018). In addition, the glycerol-choline DES showed more effective LCB pretreatment than ILs method for industrial process. But, the utilization of DESs in large scale industrial LCB pretreatment process is still need some optimized modifications.

3.1.2. Steam explosion pretreatment

The steam explosion (SE) or autohydrolysis or steam pretreatment (SP) method has extensively been studied as well as employed as one of the physico-chemical pretreatment of LCB materials (Agbor et al., 2011; Bajpai, 2016c). In SP/SE process, initially the LCB materials undergo some physical treatments such as chipping, grounding and/or simple raw preconditioning and then pretreated with high pressurized (0.7–4.8 MPa) saturated steam for several seconds to few minutes at high temperature (160–240 °C).

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

LCB resource	Deep eutectic solvent	Pretreatment 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%
Corn cob	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%
Oil palm fronds	Choline chloride–Urea	110°C, 1 h, solid to liquid ratio (1:5, w/v)	Glucose yield: 66.33 mg/ml
	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– <i>p</i> –coumaric acid	160°C, 3 h	Glucose yield: 85.7% Xylose yield: 28.8%, Delignification: 60.8%

At this experimental conditions, enhancement of the hemicellulose hydrolysis process occur, followed by liberation of such materials *i.e.*, promotion and transformation of the degraded hemicelluloses and lignins that there obviously occur upgradation of the hydrolyzed cellulose moieties into fermentable C₅ and C₆ sugar units at high temperature and pressurized medium (Agbor et al., 2011; Bajpai, 2016c). Moreover, the release of AcOH (acetic acid) from hydrolysis of hemicelluloses associated with acetyl groups in LCB materials takesplace, which may further catalyse (autocatalysis) and enhance the hydrolysis or autohydrolysis of hemicellulose moieties into fermentable glucose and xylose monomers. The optimal enzymatic hydrolysis and solubilization of hemicelluloses are favourably takenplace at lower temperature (at 190 °C) and longer residence time (at 1 min) *i.e.*, the utilization of acid catalysts such as HCl, HNO₃, H₂SO₄, CO₂ or SO₂, *etc.*, enhances the recovery of sugar moieties from hemicellulose and thereby decrease in the production of inhibitory compounds during the consequent fermentation, followed by the enzymatic hydrolysis processes (Agbor et al., 2011; Bajpai, 2016c). This pretreatment process is more efficient for hardwoods as well as agricultural residues, but less efficient for softwood materials. The main advantages of using SP method are (i) efficient and eco-friendly process, (ii) very little quantity of chemicals utilized, (iii) requirement of low energy input with low cost, *etc.* However, the main disadvantages of employing the SP approach are the partial or incomplete destruction of lignin-carbohydrate matrix (LCM), which is leading to a high threat of condensation. Also, the precipitation of soluble lignin moieties that obviously cause the LCB less digestible, destruction of xylan contents in hemicelluloses and the generation of fermentation inhibitors at very high temperatures. This process requires washing of the formed hydrolysates, during the fermentation process that eventually may lower the overall saccharification yields (20–25 %) (Agbor et al., 2011; Bajpai, 2016c).

3.1.3. Supercritical carbon dioxide explosion (Sc-CO₂) pretreatment

Currently, most of the scientists have been tried to upgrade the LCB pretreatment processes with cheaper chemicals at optimum experimental conditions (operation at lower temperature than SP treatment). in this regard the supercrititocal carbon dioxide (Sc-CO₂) pretreatment process in physico-chemical approaches has shown excellent results, when compared to other pretreatments (Ravindran and Jaiswal, 2016). Generally in Sc-CO₂ process,

the supercritical fluids are compressed at room temperature above its critical point (Ravindran and Jaiswal, 2016), thereby the $\text{CO}_{2(g)}$ molecule is the most commonly used supercritical fluid, since it is non-harmful, nonflammable, recyclable, and low-cost compound with low critical temperature and pressure (31.1 °C and 73.6 bar, respectively). Furthermore, the $\text{CO}_{2(g)}$ molecules are dissolved in H_2O to form carbonic acid, which causes very less corrosiveness. This $\text{Sc}-\text{CO}_2$ method is operated at very low temperature that helped to prevent the decomposition of sugar moieties in the presence of acidic solvents. Normally, LCB pretreatment with $\text{Sc}-\text{CO}_2$ usually leads to delignification of lignocellulosic materials. During the LCB pretreatment process, the CO_2 molecules enter into small pores of LCB materials, due to its small size (Ravindran and Jaiswal, 2016) *i.e.*, cellulosic structure is disrupted, when CO_2 pressure is released which ultimately increased the accessibility of the substrate to the cellulolytic enzymes for the process of hydrolysis.

3.1.4. Co-solvent enhanced lignocellulosic fractionation (CELf) pretreatment

In this CELf method, a mixture of tetrahydrofuran (THF) and H_2O is utilized as a monophasic solvent system and this LCB pretreatment process involves the delignification followed by conversion of glucose-rich LCB materials into high value-added fuels, including 5-HMF, FF and LA (Ashokkumar et al., 2022). CELf pretreatment technology is more effectively utilized for hardwoods, raw maple wood as well as raw corn stover. In this pretreatment process, an aqueous mixture of tetrahydrofuran (THF) with dilute mineral acids has been applied to enhance the LC biomass deconstruction *via* upholding the extensive delignification as well as solubilization of LCB with insignificant sugar degradation (Nguyen et al., 2016). This CELf method generates high percentage yields of simple fermentable sugar units and their dehydration products like 5-HMF, FF and LA, *etc.* The selection of Lewis base THF solvent in CELf methods is because of its low boiling point (66 °C), ease of recovery, recycling as well as reutilization of solvents. Application of unique polar aprotic ether as solvent with alternate to dioxane is owing to its easy coordination with both Lewis acids as well as strong Bronsted acids and simply miscible or azeotrope nature with water over a wide range of concentrations (Cai et al., 2013; Nguyen et al., 2016, 2015; Smith et al., 2016). Further, THF may be considered as a renewable solvent, which can be derived from maleic anhydride, 1,4-

butanediol or furfural that are catalytically generated from C₅ sugar moieties (Meng et al., 2018). During the CELF method, the presence of dilute mineral acids accelerate delignification process at very low temperature and also prevent the degradation of THF. At higher temperatures (at 170 °C or higher), this CELF method produces high yields of fuel precursors, comprising of FF, 5-HMF and LA, that directly from LC biomass. Also, the polar aprotic THF is associated with water and showed that it never distilled to dryness and reduced the generation of peroxide formation, as it permits safe upgrading of LCB materials for industrial applications (Smith et al., 2016). CELF method was applied to corn stover at moderate 1:1 (v/v) THF: water ratios, study showed ~ 95 % recovery of total xylose, glucose and arabinose sugar units, using only very low enzyme loadings (2 mg-protein g-glucan-in-RCS⁻¹) (Nguyen et al., 2016). About 85–95 % of acid insoluble Klason lignin materials can be removed from LC biomass, during CELF pretreatment that results in the precipitation of a very clean lignin product, also called CELF lignin, from the liquid phase after recovery of the THF by low-temperature vacuum distillation. Patri et al., studied the THF co-solvent with mineral H₂SO₄ (act as catalyst) on enzymatic hydrolysis of switchgrass biomass, yielded approximately 90 % glucose at 160 °C (Patri et al., 2021). The combining CELF pretreatment with simultaneous saccharification and fermentation (SSF) methods showed very high yields on ethanol fermentation at high LC biomass solids loadings (Cai et al., 2013; Nguyen et al., 2016, 2015).

4. Future directions

Sustainable 2G lignocellulosic derived biorefineries has been expected as an alternative to the raised growing energy crisis and environmental uncertainty. The lignocellulosic derived biofuels can be feasibly produced *via* conventional routes. Exceptionally it is in the laboratory scale level only in the aspects of certain technical as well as large-scale commercial sustainability issues and is owing to the various processing steps involved in it. In this regard, it is mandatory that development of innovative pretreatment technologies to facilitate the large-scale productivity from lignocellulosic biorefineries (Ravindran and Jaiswal, 2016; Sankaran et al., 2020). The proposed pretreatment technologies possess exclusive potentiality to get better yield along with operational flexibility from 2G lignocellulosic biomasses, further it is not at all energy-intensive for commercialization. The physical pretreatments effectively reduces size of

the components of lignocellulosic biomass materials, crystalline index of the celluloses, consequently move up the accessibility for the active sites. This technique mainly includes the mechanical shredding by means of milling & chipping (grinding), steam explosion, AFEX (ammonia based pretreatment), some radiation-based ultrasonication, γ -electron beam and microwave processes (Lu et al., 2021). The chemical pretreatment, involves degradative path of components of lignocellulosic moiety in aquatic medium by certain chemical factors namely acidic & alkaline hydrolysis, alkaline & metal salts, organo-solvents, ionic liquids (ILs) and DES (deep eutectic solvent). The physico-chemical conversion of lignocellulosic biomass components has been introduced to replace certain inconveniences caused by the both physical and chemical pretreatments towards the industrial applications. It majorly consists of extractive ammonia (EA), soaking aqueous ammonia (SAA), supercritical fluids (SCF) *viz* supercritical carbon dioxide ($Sc\text{-CO}_2$), supercritical water ($Sc\text{-H}_2\text{O}$): and supercritical ammonia ($Sc\text{-NH}_3$) explosion, LHW [liquid hot water techniques *via* hydrothermolysis & uncatalyzed solvolysis processes], SPORL (microwave assisted chemical and sulfite pretreatment) pretreatment, hydrothermal (HT) explosion and wet air oxidation to surmount the recalcitrance nature of the lignocelluloses (Moodley et al., 2020). In the case of various green bio-pretreatment pathways, which predominantly incorporate certain microorganisms *via* bacterial and fungal species for degradation of hemicelluloses as well as lignin components, by means of enhanced selective enzymatic saccharification improve both the hemicelluloses and lignins solubility to destructuralize the lignocellulose components for the enhancement in the accessibility to specific enzymes with slight environmental crash (Sankaran et al., 2020). The bio-conversion into bioenergy and high value added by-products during the different pretreatment techniques, which have been utilized in large industrial scale, till possesses considerable challenges like energy requirement, low efficiency, formation of hazardous wastes to inhibit the yield of fermentable sugars, partial degradation of cellulose and lignocelluloses *etc.* Thereby, a need of an emerging environmental friendly technique that compensates all the above mentioned challenges like necessitation of green solvents, low chemicals & energy consumption, usage in minimization of water, flexible operation with tiny particles, *etc* (Sankaran et al., 2020). A combined microwave-chemical (-acid and -alkali) pretreatment was employed to replace conventional acidic/alkaline pretreatment and it proves that the combined treatments enhance the yield of fermentable sugars quickly (Diaz et al., 2013; Singh et al., 2022). Another study recommended low-energy

ultrasonic—chemical (–alkali) pretreatment to enhance the lignocellulosic biodegradability. The Ionic liquid–ultrasound combination process with bagasse is biocompatible for cholinium IL, and it results in 80 and 72% of the celluloses and hemicelluloses saccharification process along by way of a modest inhibitory consequence on the activity of enzyme celluloses (Baruah et al., 2018). The commercial production of bio–ethanol was achieved by three pretreatment techniques viz. dil. acids, liquid hot water and AFEX. Though, in the view of techno–economical analysis, the LHW pretreatment can be considered as a commercial one (Zhao et al., 2013).

5. Critical knowledge gaps and research needs

It is challenging that ease of large–scale conversion of lignocellulosic biomass into fermentable sugars *via* different pretreatment stages is neither cost–effective nor competitive technology. Since the existence of lignin in the biomass materials inhibits the hydrolytic process of both celluloses and hemicelluloses (Baruah et al., 2018). Accordingly, wide research knowledge is required to develop different biomass pretreatment processes to delignify it. The current well–known pretreatment processes are commonly energy–intensive, in that way resourceful and cost–effective pretreatment techniques is given preference for implication in the industrial point of view (Lu et al., 2021). Recently the research reveals that acids and bases chemical pretreatment/bioconversion techniques to treat the lignocellulosic biomass feed are predictably cost–effective and commercially viable, since purified form of the by–products can obviously be reutilized as value–added products mainly drugs like compounds and optimized production of bio–ethanol (Banoth et al., 2017; Nahak et al., 2022; Sewsynker–Sukai et al., 2020). On the other hand, research gaps in knowledge on critical analyses of pretreatments can be rectified to conclude that whether the pretreatment technique is a tailor–made process to each biomass material individually and choosing particular biomasses, based on their characteristics for the best generation of bio–fuels. Also, it must be optimized to provide a single pretreatment process to perform an absolute delignification process to biomass in commercial as well as eco–friendly point of view. Further, to gain the pretreatments by dil. acidic hydrolysis in the case of scaling–up of bio–fuels production through conversion of hemicelluloses into soluble sugars is a highly efficient process and it entirely depends on various operational parameters like acid 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 biomass 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 biomass 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 sources

6. Conclusions

This critical review comprises of greener pretreatment approaches *viz.* green solvent-based ILs and DES, steam explosion, *Sc*-CO₂ 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 m³ industrial reactor *via* consequent hydrolysis. It can be suggested that the

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

CRedit authorship contribution statement

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

References

1. Agbor, V.B., Cicek, N., Sparling, R., Berlin, A., Levin, D.B., 2011. Biomass pretreatment: Fundamentals toward application. *Biotechnology Advances* 29, 675–685. <https://doi.org/10.1016/j.biotechadv.2011.05.005>
2. Agnieszka, B.–T., Florence, J.V.G., Paul, S.F., Tijs, M.L., Bennett, T., James, W., Jason, P.H., 2017. An economically viable ionic liquid for the fractionation of lignocellulosic biomass. *Green Chemistry* 19, 3078–3102. <https://doi.org/10.1039/c000000x/>
3. Ahmed, S.F., Mofijur, M., Chowdhury, S.N., Nahrin, M., Rafa, N., Chowdhury, A.T., Nuzhat, S., Ong, H.C., 2022. Pathways of lignocellulosic biomass deconstruction for biofuel and value-added products production. *Fuel* 318. <https://doi.org/10.1016/j.fuel.2022.123618>
4. Amin, F.R., Khalid, H., Zhang, H., Rahman, S. u, Zhang, R., Liu, G., Chen, C., 2017. Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express* 7, 72. <https://doi.org/10.1186/s13568-017-0375-4>
5. Amini, E., Valls, C., Roncero, M.B., 2021. Ionic liquid-assisted bioconversion of lignocellulosic biomass for the development of value-added products. *Journal of Cleaner Production* 326, 129275. <https://doi.org/10.1016/j.jclepro.2021.129275>

6. Amnuaycheewa, P., Hengaroonprasan, R., Rattanaporn, K., Kirdponpattara, S., Cheenkachorn, K., Sriariyanun, M., 2016. Enhancing enzymatic hydrolysis and biogas production from rice straw by pretreatment with organic acids. *Industrial Crops and Products* 87, 247–254. <https://doi.org/10.1016/j.indcrop.2016.04.069>
7. Anu, Kumar, A., Rapoport, A., Kunze, G., Kumar, S., Singh, D., Singh, B., 2020. Multifarious pretreatment strategies for the lignocellulosic substrates for the generation of renewable and sustainable biofuels: A review. *Renewable Energy* 160, 1228–1252. <https://doi.org/10.1016/j.renene.2020.07.031>
8. Ashokkumar, V., Venkatkarthick, R., Jayashree, S., Chuetor, S., Dharmaraj, S., Kumar, G., Chen, W.-H., Ngamcharussrivichai, C., 2022. Recent advances in lignocellulosic biomass for biofuels and value-added bioproducts – A critical review. *Bioresource Technology* 344, 126195. <https://doi.org/10.1016/j.biortech.2021.126195>
9. Bajpai, P., 2020. Chapter 7: Advantages and disadvantages of biomass utilization, in: *Biomass to Energy Conversion Technologies: The Road to Commercialization*. P. Bajpai (Ed.), Elsevier, Netherlands, pp. 169–173.
10. Bajpai, P., 2018. Wood and Fiber Fundamentals, in: *Biermann's Handbook of Pulp and Paper*. Elsevier, pp. 19–74. <https://doi.org/10.1016/B978-0-12-814240-0.00002-1>
11. Bajpai, P., 2016a. Structure of Lignocellulosic Biomass 7–12. https://doi.org/10.1007/978-981-10-0687-6_2
12. Bajpai, P., 2016b. Summary of Biomass Pretreatment Methods, in: *Pretreatment of Lignocellulosic Biomass for Biofuel Production*. Springer, Singapore, pp. 71–75. https://doi.org/10.1007/978-981-10-0687-6_5
13. Bajpai, P., 2016c. Pretreatment of Lignocellulosic Biomass, in: *Pretreatment of Lignocellulosic Biomass for Biofuel Production*. Springer, Singapore, pp. 17–70. https://doi.org/10.1007/978-981-10-0687-6_4
14. Banoth, C., Sunkar, B., Tondamanati, P.R., Bhukya, B., 2017. Improved physicochemical pretreatment and enzymatic hydrolysis of rice straw for bioethanol production by yeast fermentation. *3 Biotech* 7. <https://doi.org/10.1007/s13205-017-0980-6>
15. Baruah, J., Nath, B.K., Sharma, R., Kumar, S., Deka, R.C., Baruah, D.C., Kalita, E., 2018. Recent trends in the pretreatment of lignocellulosic biomass for value-added products. *Frontiers in Energy Research* 6, 1–19. <https://doi.org/10.3389/fenrg.2018.00141>

16. Behera, S., Arora, R., Nandhagopal, N., Kumar, S., 2014. Importance of chemical pretreatment for bioconversion of lignocellulosic biomass. *Renewable and Sustainable Energy Reviews* 36, 91–106. <https://doi.org/10.1016/j.rser.2014.04.047>
17. Bhatia, S.K., Jagtap, S.S., Bedekar, A.A., Bhatia, R.K., Patel, A.K., Pant, D., Rajesh Banu, J., Rao, C. V., Kim, Y.G., Yang, Y.H., 2020. Recent developments in pretreatment technologies on lignocellulosic biomass: Effect of key parameters, technological improvements, and challenges. *Bioresource Technology* 300, 122724. <https://doi.org/10.1016/j.biortech.2019.122724>
18. Binod, P., Satyanagalakshmi, K., Sindhu, R., Janu, K.U., Sukumaran, R.K., Pandey, A., 2012. Short duration microwave assisted pretreatment enhances the enzymatic saccharification and fermentable sugar yield from sugarcane bagasse. *Renewable Energy* 37, 109–116. <https://doi.org/10.1016/j.renene.2011.06.007>
19. Brandt, A., Gräsvik, J., Hallett, J.P., Welton, T., 2013. Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry* 15, 550–583. <https://doi.org/10.1039/c2gc36364j>
20. Brandt, A., Ray, M.J., To, T.Q., Leak, D.J., Murphy, R.J., Welton, T., 2011. Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid–water mixtures. *Green Chemistry* 13, 2489–2499. <https://doi.org/10.1039/c1gc15374a>
21. Bundhoo, Z.M.A., Mohee, R., 2018. Ultrasound–assisted biological conversion of biomass and waste materials to biofuels: A review. *Ultrasonics Sonochemistry* 40, 298–313. <https://doi.org/10.1016/j.ultsonch.2017.07.025>
22. Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E., 2013. THF co–solvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass. *Green Chemistry* 15, 3140–3145. <https://doi.org/10.1039/c3gc41214h>
23. Chandel, H., Kumar, P., Chandel, A.K., Verma, M.L., 2022. Biotechnological advances in biomass pretreatment for bio–renewable production through nanotechnological intervention. *Biomass Conversion and Biorefinery* 2024. <https://doi.org/10.1007/s13399-022-02746-0>
24. Chavan, S., Yadav, B., Atmakuri, A., Tyagi, R.D., Wong, J.W.C., Drogui, P., 2022. Bioconversion of organic wastes into value–added products: A review. *Bioresource Technology* 344. <https://doi.org/10.1016/j.biortech.2021.126398>

25. Cheah, W.Y., Sankaran, R., Show, P.L., Ibrahim, T.N.B.T., Chew, K.W., Culaba, A., Chang, J.S., 2020. Pretreatment methods for lignocellulosic biofuels production: Current advances, challenges and future prospects. *Biofuel Research Journal* 7, 1115–1127. <https://doi.org/10.18331/BRJ2020.7.1.4>
26. Chen, Z., Wan, C., 2018. Ultrafast fractionation of lignocellulosic biomass by microwave-assisted deep eutectic solvent pretreatment. *Bioresource Technology* 250, 532–537. <https://doi.org/10.1016/j.biortech.2017.11.066>
27. Dahunsi, S.O., 2019. Mechanical pretreatment of lignocelluloses for enhanced biogas production: Methane yield prediction from biomass structural components. *Bioresource Technology* 280, 18–26. <https://doi.org/10.1016/j.biortech.2019.02.006>
28. Dey, N., Kumar, G., Vickram, A.S., Mohan, M., Singhanian, R.R., Patel, A.K., Dong, C.–D., Anbarasu, K., Thanigaivel, S., Ponnusamy, V.K., 2022. Nanotechnology-assisted production of value-added biopotent energy-yielding products from lignocellulosic biomass refinery – A review. *Bioresource Technology* 344, 126171. <https://doi.org/10.1016/j.biortech.2021.126171>
29. Dharmaraja, J., Shobana, S., Arvindnarayan, S., Vadivel, M., Atabani, A.E., Pugazhendhi, A., Kumar, G., 2019. Biobutanol from lignocellulosic biomass: Bioprocess strategies. *Lignocellulosic Biomass to Liquid Biofuels* 169–193. <https://doi.org/10.1016/B978-0-12-815936-1.00005-8>
30. Diaz, A., Le Toullec, J., Blandino, A., De Ory, I., Caro, I., 2013. Pretreatment of rice hulls with alkaline peroxide to enhance enzyme hydrolysis for ethanol production. *Chemical Engineering Transactions* 32, 949–954. <https://doi.org/10.3303/CET1332159>
31. Elgharbawy, A.A., Alam, M.Z., Moniruzzaman, M., Goto, M., 2016. Ionic liquid pretreatment as emerging approaches for enhanced enzymatic hydrolysis of lignocellulosic biomass. *Biochemical Engineering Journal* 109, 252–267. <https://doi.org/10.1016/j.bej.2016.01.021>
32. Garedew, M., Lam, C.H., Petitjean, L., Huang, S., Song, B., Lin, F., Jackson, J.E., Saffron, C.M., Anastas, P.T., 2021. Electrochemical upgrading of depolymerized lignin: a review of model compound studies. *Green Chemistry* 23, 2868–2899. <https://doi.org/10.1039/d0gc04127k>
33. Halder, D., Purkait, M.K., 2021. A review on the environment-friendly emerging

- techniques for pretreatment of lignocellulosic biomass: Mechanistic insight and advancements. *Chemosphere* 264. <https://doi.org/10.1016/j.chemosphere.2020.128523>
34. Hassan, S.S., Williams, G.A., Jaiswal, A.K., 2018. Emerging technologies for the pretreatment of lignocellulosic biomass. *Bioresource Technology* 262, 310–318. <https://doi.org/10.1016/j.biortech.2018.04.099>
35. Hendriks, A.T.W.M., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology* 100, 10–18. <https://doi.org/10.1016/j.biortech.2008.05.027>
36. Henning Jørgensen, Kristensen, J.B., Felby, C., 2007. Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities. *Biofuels, Bioproducts and Biorefining* 1, 119–134. <https://doi.org/10.1002/bbb.4>
37. Hosseini Koupaie, E., Dahadha, S., Bazayr Lakeh, A.A., Azizi, A., Elbeshbishy, E., 2019. Enzymatic pretreatment of lignocellulosic biomass for enhanced biomethane production—A review. *Journal of Environmental Management* 233, 774–784. <https://doi.org/10.1016/j.jenvman.2018.09.106>
38. Jędrzejczyk, M., Soszka, E., Czapnik, M., Ruppert, A.M., Grams, J., 2019. Physical and chemical pretreatment of lignocellulosic biomass, Second and Third Generation of Feedstocks: The Evolution of Biofuels. <https://doi.org/10.1016/B978-0-12-815162-4.00006-9>
39. Kant Bhatia, S., Ahuja, V., Chandel, N., Gurav, R., Kant Bhatia, R., Govarthanan, M., Kumar Tyagi, V., Kumar, V., Pugazendhi, A., Rajesh Banu, J., Yang, Y.H., 2022. Advances in algal biomass pretreatment and its valorisation into biochemical and bioenergy by the microbial processes. *Bioresource Technology* 358, 127437. <https://doi.org/10.1016/j.biortech.2022.127437>
40. Khan, A., Vijay, R., Singaravelu, D.L., Sanjay, M.R., Siengchin, S., Jawaid, M., Alamry, K.A., Asiri, A.M., 2022. Extraction and Characterization of Natural Fibers from *Citrullus lanatus* Climber. *Journal of Natural Fibers* 19, 621–629. <https://doi.org/10.1080/15440478.2020.1758281>
41. Khan, M.U., Usman, M., Ashraf, M.A., Dutta, N., Luo, G., Zhang, S., 2022. A review of recent advancements in pretreatment techniques of lignocellulosic materials for biogas production: Opportunities and Limitations. *Chemical Engineering Journal Advances* 10,

100263. <https://doi.org/10.1016/j.cej.2022.100263>
42. Kumar, B., Bhardwaj, N., Agrawal, K., Chaturvedi, V., Verma, P., 2020. Current perspective on pretreatment technologies using lignocellulosic biomass: An emerging biorefinery concept. *Fuel Processing Technology* 199. <https://doi.org/10.1016/j.fuproc.2019.106244>
43. Kumar, G., Dharmaraja, J., Arvindnarayan, S., Shoban, S., Bakonyi, P., Saratale, G.D., Nemestóthy, N., Bélafi-Bakó, K., Yoon, J.J., Kim, S.H., 2019. A comprehensive review on thermochemical, biological, biochemical and hybrid conversion methods of bio-derived lignocellulosic molecules into renewable fuels. *Fuel* 251, 352–367. <https://doi.org/10.1016/j.fuel.2019.04.049>
44. Li, L., Zhao, Y., Lian, W., Han, C., Zhang, Q., Huang, W., 2021. Review on the effect of heat exchanger tubes on flow behavior and heat/mass transfer of the bubble/slurry reactors. *Chinese Journal of Chemical Engineering* 35, 44–61. <https://doi.org/10.1016/j.cjche.2021.03.017>
45. Li, M., Pu, Y., Ragauskas, A.J., 2016. Current understanding of the correlation of lignin structure with biomass recalcitrance. *Frontiers in Chemistry* 4, 1–8. <https://doi.org/10.3389/fchem.2016.00045>
46. Loow, Y.L., Wu, T.Y., Yang, G.H., Ang, L.Y., New, E.K., Siow, L.F., Md. Jahim, J., Mohammad, A.W., Teoh, W.H., 2018. Deep eutectic solvent and inorganic salt pretreatment of lignocellulosic biomass for improving xylose recovery. *Bioresource Technology* 249, 818–825. <https://doi.org/10.1016/j.biortech.2017.07.165>
47. Lorenci Woiciechowski, A., Dalmas Neto, C.J., Porto de Souza Vandenberghe, L., de Carvalho Neto, D.P., Novak Sydney, A.C., Letti, L.A.J., Karp, S.G., Zevallos Torres, L.A., Soccol, C.R., 2020. Lignocellulosic biomass: Acid and alkaline pretreatments and their effects on biomass recalcitrance – Conventional processing and recent advances. *Bioresource Technology* 304, 122848. <https://doi.org/10.1016/j.biortech.2020.122848>
48. Lu, F., Wang, C., Chen, M., Yue, F., Ralph, J., 2021. A facile spectroscopic method for measuring lignin content in lignocellulosic biomass. *Green Chemistry* 23, 5106–5112. <https://doi.org/10.1039/d1gc01507a>
49. Lugani, Y., Rai, R., Prabhu, A.A., Maan, P., Hans, M., Kumar, V., Kumar, S., Chandel, A.K., Sengar, R.S., 2020. Recent advances in bioethanol production from lignocelluloses:

- a comprehensive review with a focus on enzyme engineering and designer biocatalysts. *Biofuel Research Journal* 7, 1267–1295. <https://doi.org/10.18331/BRJ2020.7.4.5>
50. Mankar, A.R., Pandey, A., Modak, A., Pant, K.K., 2021. Pretreatment of lignocellulosic biomass: A review on recent advances. *Bioresource Technology* 334, 125235. <https://doi.org/10.1016/j.biortech.2021.125235>
51. Meng, X., Parikh, A., Seemala, B., Kumar, R., Pu, Y., Christopher, P., Wyman, C.E., Cai, C.M., Ragauskas, A.J., 2018. Chemical Transformations of Poplar Lignin during Cosolvent Enhanced Lignocellulosic Fractionation Process. *ACS Sustainable Chemistry and Engineering* 6, 8711–8718. <https://doi.org/10.1021/acssuschemeng.8b01028>
52. Moodley, P., Sewsynker-Sukai, Y., Gueguim Kana, E.B., 2020. Progress in the development of alkali and metal salt catalysed lignocellulosic pretreatment regimes: Potential for bioethanol production. *Bioresource Technology* 310, 123372. <https://doi.org/10.1016/j.biortech.2020.123372>
53. Muharja, M., Junianti, F., Ranggina, D., Nurtono, T., Widjaja, A., 2018. An integrated green process: Subcritical water, enzymatic hydrolysis, and fermentation, for biohydrogen production from coconut husk. *Bioresource Technology* 249, 268–275. <https://doi.org/10.1016/j.biortech.2017.10.024>
54. Nahak, B.K., Preetam, S., Sharma, D., Shukla, S.K., Syväjärvi, M., Toncu, D.C., Tiwari, A., 2022. Advancements in net-zero pertinency of lignocellulosic biomass for climate neutral energy production. *Renewable and Sustainable Energy Reviews* 161. <https://doi.org/10.1016/j.rser.2022.112393>
55. New, E.K., Tnah, S.K., Voon, K.S., Yong, K.J., Procentese, A., Yee Shak, K.P., Subramonian, W., Cheng, C.K., Wu, T.Y., 2022. The application of green solvent in a biorefinery using lignocellulosic biomass as a feedstock. *Journal of Environmental Management* 307. <https://doi.org/10.1016/j.jenvman.2021.114385>
56. Nguyen, T.Y., Cai, C.M., Kumar, R., Wyman, C.E., 2015. Co-solvent Pretreatment Reduces Costly Enzyme Requirements for High Sugar and Ethanol Yields from Lignocellulosic Biomass. *ChemSusChem* 8, 1716–1725. <https://doi.org/10.1002/cssc.201403045>
57. Nguyen, T.Y., Cai, C.M., Osman, O., Kumar, R., Wyman, C.E., 2016. CELF pretreatment of corn stover boosts ethanol titers and yields from high solids SSF with low

- enzyme loadings. *Green Chemistry* 18, 1581–1589. <https://doi.org/10.1039/c5gc01977j>
58. Nimmanterdwong, P., Chalermnsinsuwan, B., Piumsomboon, P., 2021. Prediction of lignocellulosic biomass structural components from ultimate/proximate analysis. *Energy* 222, 119945. <https://doi.org/10.1016/j.energy.2021.119945>
59. Patri, A.S., Mohan, R., Pu, Y., Yoo, C.G., Ragauskas, A.J., Kumar, R., Kisailus, D., Cai, C.M., Wyman, C.E., 2021. THF co-solvent pretreatment prevents lignin redeposition from interfering with enzymes yielding prolonged cellulase activity. *Biotechnology for Biofuels* 14, 1–13. <https://doi.org/10.1186/s13068-021-01904-2>
60. Procentese, A., Raganati, F., Olivieri, G., Russo, M.E., Rehmann, L., Marzocchella, A., 2018. Deep Eutectic Solvents pretreatment of agro-industrial food waste. *Biotechnology for Biofuels* 11, 1–12. <https://doi.org/10.1186/s13068-018-1034-y>
61. Raj, T., Chandrasekhar, K., Naresh Kumar, A., Kim, S.H., 2022. Lignocellulosic biomass as renewable feedstock for biodegradable and recyclable plastics production: A sustainable approach. *Renewable and Sustainable Energy Reviews* 158, 112130. <https://doi.org/10.1016/j.rser.2022.112130>
62. Rasool, T., Najar, I., Srivastava, V.C., Pandey, A., 2021. Pyrolysis of almond (*Prunus amygdalus*) shells: Kinetic analysis, modelling, energy assessment and technical feasibility studies. *Bioresource Technology* 337, 125466. <https://doi.org/10.1016/j.biortech.2021.125466>
63. Ravindran, R., Jaiswal, A.K., 2016. A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: Challenges and opportunities. *Bioresource Technology* 199, 92–102. <https://doi.org/10.1016/j.biortech.2015.07.106>
64. Rebello, S., Anoopkumar, A.N., Aneesh, E.M., Sindhu, R., Binod, P., Pandey, A., 2020. Sustainability and life cycle assessments of lignocellulosic and algal pretreatments. *Bioresource Technology* 301. <https://doi.org/10.1016/j.biortech.2019.122678>
65. Salakkam, A., Plangklang, P., Sittijunda, S., Boonmee Kongkeitkajorn, M., Lunprom, S., Reungsang, A., 2019. Chapter 6: Bio-hydrogen and Methane Production from Lignocellulosic Materials, in: Abomohra, A.E.–F. (Ed.), *Biomass for Bioenergy – Recent Trends and Future Challenges*. IntechOpen, London, United Kingdom, p. 126195. <https://doi.org/10.5772/intechopen.85138>
66. Sankaran, R., Parra Cruz, R.A., Pakalapati, H., Show, P.L., Ling, T.C., Chen, W.H., Tao,

- Y., 2020. Recent advances in the pretreatment of microalgal and lignocellulosic biomass: A comprehensive review. *Bioresource Technology* 298, 122476. <https://doi.org/10.1016/j.biortech.2019.122476>
67. Sewsynker–Sukai, Y., Naomi David, A., Gueguim Kana, E.B., 2020. Recent developments in the application of kraft pulping alkaline chemicals for lignocellulosic pretreatment: Potential beneficiation of green liquor dregs waste. *Bioresource technology* 306, 123225. <https://doi.org/10.1016/j.biortech.2020.123225>
68. Sharma, V., Tsai, M.L., Chen, C.W., Sun, P.P., Patel, A.K., Singhania, R.R., Nargotra, P., Dong, C. Di, 2022. Deep eutectic solvents as promising pretreatment agents for sustainable lignocellulosic biorefineries: A review. *Bioresource Technology* 360. <https://doi.org/10.1016/j.biortech.2022.127631>
69. Shirkavand, E., Baroutian, S., Gapes, D.J., Young, B.R., 2016. Combination of fungal and physicochemical processes for lignocellulosic biomass pretreatment – A review. *Renewable and Sustainable Energy Reviews* 54, 217–234. <https://doi.org/10.1016/j.rser.2015.10.003>
70. Singh, H., Tomar, S., Qureshi, K.A., Jaremko, M., Rai, P.K., 2022. Recent Advances in Biomass Pretreatment Technologies for Biohydrogen Production. *Energies* 15, 1–22. <https://doi.org/10.3390/en15030999>
71. Smith, M.D., Mostofian, B., Cheng, X., Petridis, L., Cai, C.M., Wyman, C.E., Smith, J.C., 2016. Cosolvent pretreatment in cellulosic biofuel production: Effect of tetrahydrofuran–water on lignin structure and dynamics. *Green Chemistry* 18, 1268–1277. <https://doi.org/10.1039/c5gc01952d>
72. Solarte–Toro, J.C., Romero–García, J.M., Martínez–Patiño, J.C., Ruiz–Ramos, E., Castro–Galiano, E., Cardona–Alzate, C.A., 2019. Acid pretreatment of lignocellulosic biomass for energy vectors production: A review focused on operational conditions and techno–economic assessment for bioethanol production. *Renewable and Sustainable Energy Reviews* 107, 587–601. <https://doi.org/10.1016/j.rser.2019.02.024>
73. Thanigaivel, S., Priya, A.K., Dutta, K., Rajendran, S., Sekar, K., Jalil, A.A., Soto–Moscoso, M., 2022. Role of nanotechnology for the conversion of lignocellulosic biomass into biopotent energy: A biorefinery approach for waste to value–added products. *Fuel* 322, 124236. <https://doi.org/10.1016/j.fuel.2022.124236>

74. Tian, S.Q., Zhao, R.Y., Chen, Z.C., 2018. Review of the pretreatment and bioconversion of lignocellulosic biomass from wheat straw materials. *Renewable and Sustainable Energy Reviews* 91, 483–489. <https://doi.org/10.1016/j.rser.2018.03.113>
75. Tu, W.C., Hallett, J.P., 2019. Recent advances in the pretreatment of lignocellulosic biomass. *Current Opinion in Green and Sustainable Chemistry* 20, 11–17. <https://doi.org/10.1016/j.cogsc.2019.07.004>
76. Ummalyma, S.B., Supriya, R.D., Sindhu, R., Binod, P., Nair, R.B., Pandey, A., Gnansounou, E., 2019. Biological pretreatment of lignocellulosic biomass—current trends and future perspectives, *Second and Third Generation of Feedstocks: The Evolution of Biofuels*. Elsevier Inc. <https://doi.org/10.1016/B978-0-12-815162-4.00007-0>
77. Usmani, Z., Sharma, M., Gupta, P., Karpichev, Y., Gathergood, N., Bhat, R., Gupta, V.K., 2020. Ionic liquid based pretreatment of lignocellulosic biomass for enhanced bioconversion. *Bioresource Technology* 304, 123003. <https://doi.org/10.1016/j.biortech.2020.123003>
78. Yadav, M., Paritosh, K., Vivekanand, V., 2020. Lignocellulose to bio-hydrogen: An overview on recent developments. *International Journal of Hydrogen Energy* 45, 18195–18210. <https://doi.org/10.1016/j.ijhydene.2019.10.027>
79. Yoo, C.G., Meng, X., Pu, Y., Ragauskas, A.J., 2020. The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review. *Bioresource Technology* 301, 122784. <https://doi.org/10.1016/j.biortech.2020.122784>
80. Yoo, C.G., Pu, Y., Ragauskas, A.J., 2017. Ionic liquids: Promising green solvents for lignocellulosic biomass utilization. *Current Opinion in Green and Sustainable Chemistry* 5, 5–11. <https://doi.org/10.1016/j.cogsc.2017.03.003>
81. Yousuf, A., Pirozzi, D., Sannino, F., 2019. Fundamentals of lignocellulosic biomass. *Lignocellulosic Biomass to Liquid Biofuels* 1–15. <https://doi.org/10.1016/B978-0-12-815936-1.00001-0>
82. Zhang, J., Zhang, X., Yang, M., Singh, S., Cheng, G., 2021. Transforming lignocellulosic biomass into biofuels enabled by ionic liquid pretreatment. *Bioresource Technology* 322. <https://doi.org/10.1016/j.biortech.2020.124522>
83. Zhao, W., Zhang, Y., Du, B., Wei, D., Wei, Q., Zhao, Y., 2013. Enhancement effect of

- 968 silver nanoparticles on fermentative biohydrogen production using mixed bacteria.
969 Bioresource Technology 142, 240–245. <https://doi.org/10.1016/j.biortech.2013.05.042>
970 84. Zoghلامي, A., Paës, G., 2019. Lignocellulosic Biomass: Understanding Recalcitrance and
971 Predicting Hydrolysis. Frontiers in Chemistry 7, 874.
972 <https://doi.org/10.3389/fchem.2019.00874>

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 ($Sc\text{-CO}_2$) has been documented.



DSSPACE

<https://dspace.org/>

Lignocellulosic biomass conversion via greener pretreatment methods towards biorefinery applications

Dharmaraja, Jeyaprakash; Shobana, Sutha; Arvindnarayan, Sundaram; Francis, Rusal Raj; Jeyakumar, Rajesh Banu ...

2022-11-28

Elsevier

<https://doi.org/10.1016/j.biortech.2022.128328>

Dharmaraja J, Shobana S, Arvindnarayan S, et al., (2023) Lignocellulosic biomass conversion via greener pretreatment methods towards biorefinery applications. Bioresource Technology, Volume 369, February 2023, Article number 128328