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Lignocellulosic Biomass Conversion *via* Greener Pretreatment Methods towards biorefinery applications

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

Keywords: *Lignocellulose; Pretreatments; ILs; DES; Sc–CO_2; CELF.*

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1. Introduction

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

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

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–chemcial 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 enzyems 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*–CO_2) and co–solvent enhanced lignocellulosic fractionation (CELF) 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 strucrure 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).

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

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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	
C. odorata (Siam weed)	41.00	17.30	20.70	
Elephant grass	47.12	36.01	11.50	
Eichhornia crassipes	18.20	48.70	3.50	
Ensiled grass	37.90	27.30	9.70	
Hemp	53.86	10.60	8.76	
	68.00	15.00	10.00	
Lantana camara	45.10	17.00	27.30	
Meadow grass	41.28	28.14	30.14	
Napier grass	47.00	31.00	22.00	
	45.70	33.70	20.60	
Naturally hay	44.90	31.40	12.00	
Orchard grass	52.30	42.90	6.60	
Reed	49.40	31.50	8.74	
	39.50	29.80	24.00	
Rye	42.83	27.86	6.51	
Saccharum spontaneum	45.10	22.80	24.40	
Silage	39.27	25.96	9.02	
Smooth brome grass	49.80	41.90	7.60	
Sunflower	34.06	5.18	7.72	
Switchgrass	26.80–37.50	22.40–28.80	13.20–22.50	
Szarvasi–1	37.85	27.33	9.65	
Tall fescue	23.40–26.40	18.20–20.40	10.90–14.80	
Verge grass	30.70	15.60	14.10	
Hardwood				(Ashokkumar et al., 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	
Pinus armandii Franch	48.40	17.80	24.10	
Spruce wood	24.70	10.20	35.00	
	29.00	30.00	22.80	
	43.00	29.40	27.60	
	45.50	22.90	27.90	
Sawdust				(Ashokkumar et al.,
Gmelina arborea sawdust	23.00	–	23.30	2022; Ummalyma et
Salvadora oleoides saw dust	24.00	–	21.80	al., 2019)
Willow sawdust	35.60	21.50	28.70	
Agricultural and food processing industry wastes				(Agbor et al., 2011;
Apple pomace	8.810	5.440	2.98	Amini et al., 2021;
Acacia pruning	44.90	13.00	32.00	Ashokkumar et al.,
Almond shell	27.00	30.00	36.00	2022; Dharmaraja et
Bamboo	46.50	18.80	25.70	al., 2019; Haldar and
	45–50	18–20	23.00	Purkait, 2021;
	26–43	15–26	21–31	Hassan et al., 2018;
Bamboo leaves	34.14	25.55	35.03	A. Khan et al., 2022;
Banana waste	13.20	14.80	14.00	New et al., 2022; Raj
Banana peel	12.17	10.19	2.88	et al., 2022;
	11.45	25.52	9.82	Sewsynker–Sukai et
Barley straw	35.40	28.70	13.10	al., 2020; Usmani et
	45.00	38.00	19.00	al., 2020; Yoo et al.,
	36.00–43.00	24.00–33.00	6.30–13.10	2017)
Barley hull	34.00	36.00	13.80–19.00	
Carrot pomace	28.00	6.70	17.50	
	10.01	5.73	2.50	

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

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

The long chain polymers that are packed into macrofibrils and these macrofibrils are covered by hemicellulose and lignin contents. The formed fibrils are highly microcrystalline (50–90 %) with linear structure however, 10–45 % existence of the amorphous regions is due to random orientation of structural units. The formation of fermentable simple D–glucose unit from the cellulose *via* either mineral acid or enzymes break the (*β*–1–4)–glycosidic bonds (Bajpai, 2018, 2016a; Bhatia et al., 2020; Lorenci Woiciechowski et al., 2020; Mankar et al., 2021). The 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 C_5 (*β*–D–xylose &*α*–L–arabinose) and C_6 (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*–*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 C_5 and C_6 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 [($C_{10}H_{11}O_{3.5}$); 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; Zoghlami 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; Zoghlami 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*–1and *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). Furthemore, 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 pretretamnet technology should be attentive in vein 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 breakingdown 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 cavitational effect on principle of ultrasound radiation technology is widely being applied on LCB pretreatment process that leads to breakdown the lingnin 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 utilizatilation of the physical pretreatment is the energy consumption (Tu and Hallett, 2019). Furtrher, this physical tehnology 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, H_2SO_4, HNO_3, *etc.,* and organic oxalic, maleic, succinic acids, *etc*), alkaline or base hydrolysis (KOH, NaOH, Na_2CO_3, CaO, $CaCO_3/Ca(OH)_2$, NH_3, *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 C_5 and C_6 sugar units, which are convereted 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/freeze 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 provid an efficient and expected LCB degradability results. So, the combined pretreatment processes, which are integrating two or more pretreatment tehnologies 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 feasiblly 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 steram pretreatment (SP), supercritical carbon dioxide explosion (*Sc*–CO_2), 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 milling, Crushing, Cutting, Shredding)	Reduce the particle size and disrupt the crystallinity	Control of final particle size, easy handling, less waterconsumption, free from chemical intake, increased surface area, low production cost	High energy consumption than inherent biomass energy, low release of sugar content, commercial feasilbility is very less, inability to remove lignin which restricts the access of the enzymes to cellulose and inhibit cellulases
Irradiation (Microwave and Ultrasound)	Swelling andfragmentation oflignocellulosicmaterial	Fast heat transfer, shortreaction time, energyefficient, cheap and generate less / no pollution, increased porosity, highly efficient at batch scale, dissolve extractives with heating	Low penetration of radiationin bulk products, distribution of microwavepower around of LCB dueto non–homogeneous material, high energy consumption than inherent biomass energy, low release of sugar content, commercial feasilbility is very less
Chemical pretreatment			
Acid hydrolysis (using dilute or concentrated acids, organic acids)	Lignin cellulose and hemicellulose fractionate	Enzymatic hydrolysis not required the acid, hydrolyzes the hemicellulose into xylose and other sugars, alters lignin structure, increase in porosity, increased enzymatic hydrolysis, commercial feasible, high enzymatic yield, increased cellulose crystallinity, short retention time	Concnetrated acid process is corrosive and toxic, formation of inhibitors at low pH& pseudo lignin as by–products, high cost, equipment corrosion,formation of toxic substances at higher severity, need acid neutralization, toxin formation at higher severity, requirement high metallurgy, pseudo lignin formation, cellulose crystallinity enhancement
Base or Alkaline hydrolysis	Lignin and hemicellulose removal	Reduce the absorption of cellulose due to efficient lignin removal, low cost, utilize lower temperatures and	Generates inhibitors, long residence time required, less effective as lignin content of the biomass increases, treatment of a large

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

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

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3.1.1. Novel green solvent–based ILs and DES pretreatments

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

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

Butyl–3–methylimidazolium iodide,[Bmim]$MeSO_4$: 1–Butyl–3–methylimidazolium methylsulfate, [BmPy]Cl: 1–Butyl–3–methylpyridinium chloride, [C_4C_1im][$MeSO_4$]: 1,3–dimethylimidazoliummethyl sulfate, [C_4C_1im][HSO_4]: 1–butyl–3–methylimidazolium hydrogensulfate, [C_4Him][HSO_4]: 1–butylimidazolium hydrogen sulfate, [C_4C_1im]Cl: 1–butyl–3–methylimidazolium chloride, [C_4C_1im][$MeCO_2$]: 1–Butyl–3–methylimidazolium acetate, [Emim]OAc: 1–Ethyl–3–methylimidazolium acetate,[Emim]Cl: 1–Ethyl–3–methylimidazolium chloride, [Hmim]CF_3SO_3: 1–Hexyl–3 methylimidazolium trifluoromethanesulfonate, [Mmim]$MeSO_4$: 1,3–Dimethylimidazolium methylsulfate, [MBPcl]: 3–methyl–N–bytylpyridinium 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 [C_4C_1im][$MeSO_4$], [C_4C_1im][HSO_4], [C_4Him][HSO_4], [C_4C_1im]Cl, [C_4C_1im][$MeCO_2$], *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][HSO_4]$^-$ and 1–butyl–3–methylimidazolium methyl sulfate [Bmim][CH_3SO_4] (Brandt et al., 2011). It showed that >9 0% 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.

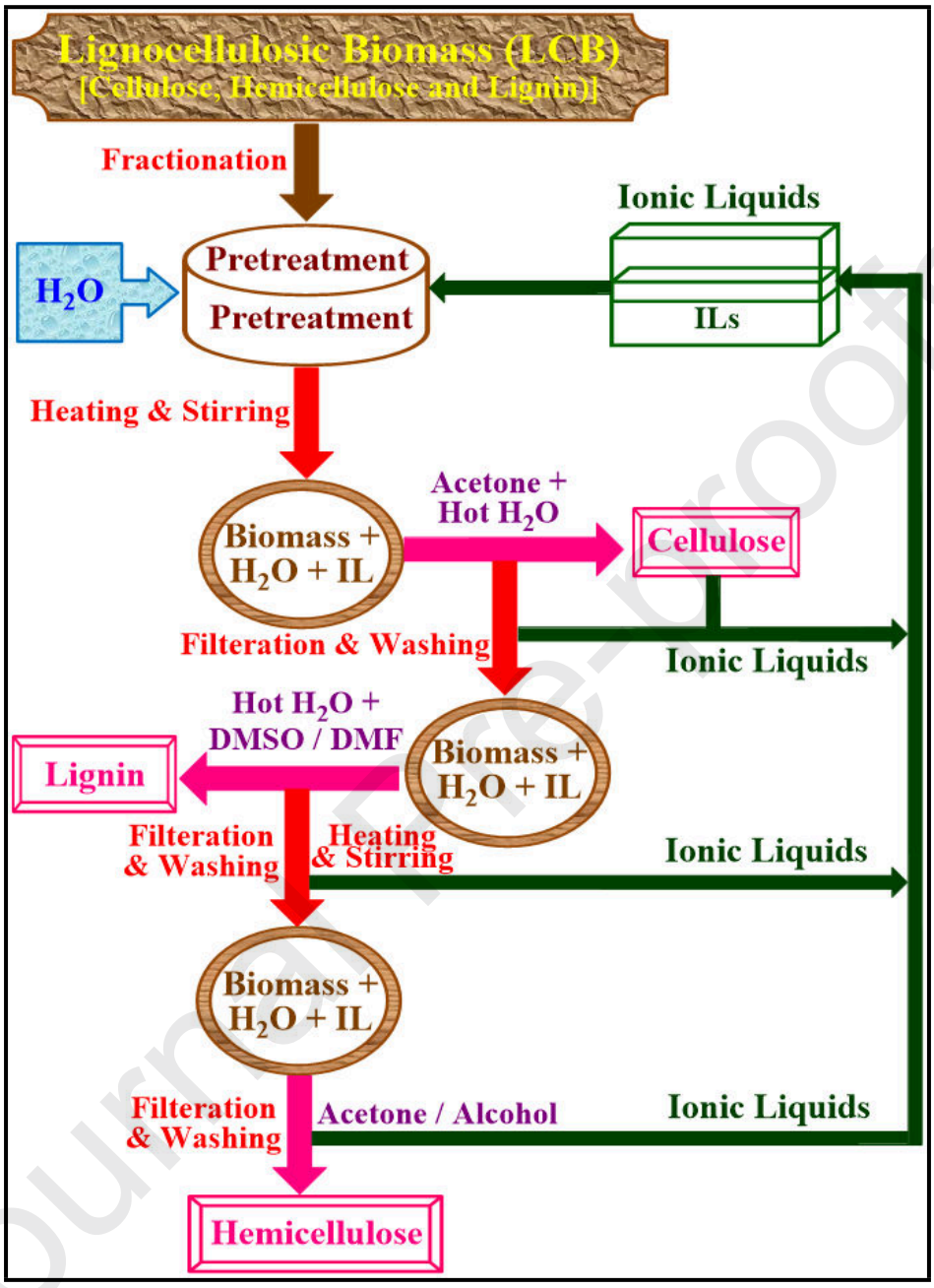


Fig. 1. LCB pretreatment process with ILs [Adopted and modified Ref. (Usmani et al., 2020)].

396 Table 3. Various LCB material sources under ILs pretreatement process and the yields of cellulose and lignin contents (wt
397 %) [Adopted and modified Ref. (Usmani et al., 2020)].
398

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_2SiO_3	Whirlpool mixer	1 g/20 g	1 h	120	96.80
Soyabean straw	[Bmim][Cl]	Whirlpool mixer	1 g/20 g	1 h	120	96.50
Rice Straw	[Emim][OAc]–DMSO (1:1)	Preheated using oil bath	50 mg / ml	10 min	80	28.00
	[Emim][OAc]–DMA (1:1)				80	28.00
	[Emim][DMP]–DMSO (1:1)				80	24.00
For lignin						
Miscanthus Pulp	[triethylammonium][HSO_4]	Convection	1 g / 20 g	8 h	120	20.00
Pine	[Bmim][$MeCO_2$]	–	1 g / 10 g	22 h	120	26.23
Pine Pulp	[triethylammonium][HSO4]	Convection	1 g / 10 g	8 h	120	5.00
Pine Pulp (Indulin)	[Ch][OAc]	–	5 mg / g	3 h	90	28.00

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	[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_2O]–[Bmim][HSO_4]		Stainless Steel Reactor	1 g / 30 ml	30 min	90	24.06 ± 2.65
Poplar	[1,4–Butylene Glycol/H_2O]–[Bmim][HSO_4]		Stainless Steel Reactor	1 g / 30 ml	30 min	90	11.12 ± 3.34
Coconut Shell	[Bmim][OAc]		Heating Block (N_2)	10 mg / g	2 h	150	8.60
	[Emim][OAc]						10.30
Switchgrass	[Bmim][PF_6]		–	15 g / 135 g	3 h	160	65.00
Eucalyptus	[Bmim][OAc]		–	5 g / 100 g	30 min	120	16.97
Oil palm frond	[Emim][DEP]		Round–bottom flask	1 g / 10 g	4 h	90 oil bath	13.00 ± 0.50
Oil palm biomass	[Bmim][Cl]		Rotary Evaporator	1 g / 10 g	8 h	110	22.78 ± 1.47
Bamboo biomass	[Emim][OAc]		–	0.5 g / 10 g	2 h	90	24.30 ± 0.80
						110	19.00 ± 1.20
						130	17.90 ± 1.00

[a][Bmim][OAc]: 1–butyl–3–methylimidazolium acetate; [Bmim][PF_6]: 1–butyl–3–methylimidazolium hexafluorophosphate; [BMPy][Cl]: 1–butyl–3–methylpyridinium chloride; [BMPyr][$N(CN)_2$]: 1–butyl–1–methylpyrrolidinium; [Ch][OAc]: Cholinium acetate; DMA: Dimethylacetamide; DMSO: Diethyl sulfoxide; [Emim][DMP]: 1–Ethyl–3–methylimidazolium dimethyl phosphate; [Emim][DEP]: 1–Ethyl–3–methylimidazolium diethyl phosphate.

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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 performence, 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 ultilization of DESs in large scale industrial LCB pretreatment process is still need some optimized modifications.

3.1.2. Steam expolsion 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 ^{o}C).

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

LCB resource	Deep eutectic solvent	Pretreatement conditions	Effect on saccharification
Corn stover	Choline chloride–Formic acid	130°C, 2h, solid loading (5% w/v)	Glucose yield: 99% Lignin removal: 23.8%
Corncob	Choline chloride–Imidazole	115°C, 15 h, solid to liquid ratio (1:16, w/v)	Glucose yield: 94% Xylose yield: 84%
Eucalyptus saw dust	Choline chloride–lactic acid	110°C, 6 h, solid loading (10%, w/v)	Hydrolysis yield: 94.3% Delignification 80%
Lettuce residue	Choline chloride–glycerol	150°C, 16 h, solid:liquid ratio (1:16, w/v)	Glucose yield: 94.9% Xylose yield: 75.0%
Oil palm empty fruit bunch	Choline chloride–lactic acid	120°C, 3 h, solid to liquid ratio (1:10, w/v)	Reducing sugars yield: 20.7%
	Choline chloride–Urea	110°C, 1 h, solid to liquid ratio (1:5, w/v)	Glucose yield: 66.33 mg/ml
Oil palm fronds	Choline chloride–Urea–$CuCl_2$	120°C, 30 min, solid loading (10%, w/v)	Xylose yield: 14.76 g/L
Rice straw, rice husk, and wheat straw	Choline chloride–Oxalic acid–n–butanol	120°C, 1 h, solid loading (15%, w/v)	Delignification:50%
Rice husk	Ethylene glycol–choline chloride	160°C, 4 h, solid loading (4%, w/v)	Reducing sugar yield: 0.74 mg/mL
Rice straw	Potassium carbonate–glycerol	140°C, 100 min, solid to liquid ratio (1:10, w/v)	Enhanced delignification
Switchgrass	Choline chloride–*p*–coumaric acid	160°C, 3 h	Glucose yield: 85.7% Xylose yield: 28.8%, Delignification: 60.8%

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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 C_5 and C_6 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 ^oC) and longer residence time (at 1 min) *i.e.,* the utilization of acid catalysts such as HCl, HNO_3, H_2SO_4, CO_2 or SO_2, *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. Aslo, 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*–CO_2) 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*–CO_2) pretreatment process in physico–chemical approaches has shown excellent results, when compared to other pretreatments (Ravindran and Jaiswal, 2016). Generally in *Sc*–CO_2 process,

the supercritical fluids are compressed at roomtemperature above its critical point (Ravindran and Jaiswal, 2016), thereby the $CO_{2(g)}$ 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 $CO_{2(g)}$ molecules are dissolved in H_2O to form carbonic acid, which causes very less corrosiveness. This *Sc*–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 *Sc*–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 ^oC), 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 C_5 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 ^{o}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 H_2SO_4 (act as catalyst) on enzymatic hydrolysis of switchgrass biomass, yielded approximately 90 % glucose at 160 ^{o}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

565 the components of lignocellulosic biomass materials, crystalline index of the celluloses,
566 consequently move up the accessibility for the active sites. This technique mainly includes the
567 mechanical shredding by means of milling & chipping (grinding), steam explosion, AFEX
568 (ammonia based pretreatment), some radiation–based ultrasonication, *γ*–electron beam and
569 microwave processes (Lu et al., 2021). The chemical pretreatment, involves degradative path of
570 components of lignocellulosic moiety in aquatic medium by certain chemical factors namely
571 acidic & alkaline hydrolysis, alkaline & metal salts, organo–solvents, ionic liquids (ILs) and
572 DES (deep eutectic solvent). The physico–chemical conversion of lignocellulosic biomass
573 components has been introduced to replace certain inconveniencies caused by the both physical
574 and chemical pretreatments towards the industrial applications. It majorly consists of extractive
575 ammonia (EA), soaking aqueous ammonia (SAA), supercritical fluids (SCF) *viz* supercritical
576 carbon dioxide (*Sc*–CO_2), supercritical water (*Sc*–H_2O): and supercritical ammonia (*Sc*–NH_3)
577 explosion, LHW [liquid hot water techniques *via* hydrothermolysis & uncatalyzed solvolysis
578 processes], SPORL (microwave assisted chemcial and sulfite pretreatment) pretreatment,
579 hydrothermal (HT) explosion and wet air oxidation to surmount the recalcitrance nature of the
580 lignocelluloses (Moodley et al., 2020). In the case of various green bio–pretreatment pathways,
581 which predominantly incorporate certain microorganisms *via* bacterial and fungal species for
582 degradation of hemicelluloses as well as lignin components, by means of enhanced selective
583 enzymatic saccharification improve both the hemicelluloses and lignins solubility to
584 destructuralize the lignocellulose components for the enhancement in the accessiblity to specific
585 enzymes with slight environmental crash (Sankaran et al., 2020). The bio–conversion into
586 bioenergy and high value added by–products during the different pretreatment techniques, which
587 have been utilized in large industrial scale, till possesses considerable challenges like energy
588 requirement, low efficiency, formation of hazardous wastes to inhibit the yield of fermentable
589 sugars, partial degradation of cellulose and lignocelluloses *etc*. Thereby, a need of an emerging
590 environmental friendly technique that compensates all the above mentioned challenges like
591 necessitation of green solvents, low chemicals & energy consumption, usage in minimization of
592 water, flexible operation with tiny particles, *etc* (Sankaran et al., 2020). A combined microwave–
593 chemical (–acid and –alkali) pretreatment was employed to replace conventional acidic/alkaline
594 pretreatment and it proves that the combined treatments enhance the yield of fermentable sugars
595 quickly (Diaz et al., 2013; Singh et al., 2022). Another study recommended low–energy

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* ifferent 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 chosing 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

627 gathered (Sankaran et al., 2020). Simultaneously, the knowledge to provide production of certain
628 inhibitors like furfural and phenolics, *etc*., prevention of these toxic compounds can be
629 performed by means of choice of lignocellulosic biomasss material and a simple strategy that
630 would be lying on the fact that cautious application of mild pretreatments. In the case of
631 enzymatic pretreatment, the complete removal of toxic compounds can be performed by
632 employment of certain enzymes like laccase, peroxidases, *etc*. The combined structure of
633 pretreatment techniques and enzymatic hydrolysis are often more effective performances and
634 such techniques majorly depend on choice, while handling the biomasses kinds (Ravindran and
635 Jaiswal, 2016). Consequently, this lignin components have been consumed for the commercial
636 production of high–value added materials by means of direct combustion to provide adequate
637 energy for industrial purposes. In this view, fast pyrolytic procedure is currently becoming
638 accustomed by the interest of researchers as it possesses the potentiality to the effective
639 conversion of lignin to high commercially value added products like bio–char, bio–oil, *etc*. But
640 the production of gaseous phase bio–fuels for the industrial purpose, a well defined particular
641 approach is necessary to comprehensively analyze the overall operation cost. In such a way that
642 the the research knowledge provides ease of production of bio–H and some other bio–fuels from
643 lignocellulosic biomass materials is simple *via* these processes by producing simple bio–
644 molecules (Sankaran et al., 2020). Furthermore, the ease of production of biogas *via* anaerobic
645 digestion, frequently is one of the heat generating integrated processes. . Additionally, the
646 research knowledge on such techniques proffer high–digestible biomass feed apart from the fact
647 that recycling, recovery and consumption of so produced solids and liquids from the wastewater
648 souces
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650 **6. Conclusions**
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652 This critical review comprises of greener pretreatment approaches *viz*. green solvent–
653 based ILs and DES, steam expolsion, *Sc*–CO_2 and CELF pretreatments for various
654 lignocellulosic biomass materials. Further, the steam explosion can be considered as a core
655 technology for agricultural residues–derived bio–fuel production in industrial scale since it was
656 revealed that corn–stover yields 80 and > 90 % of hemicelluloses and celluloses, respectively in
657 a 50 m^3 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.

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Highlights

- Structural composition of lignocellulose biomass was provided.
- Advanced green pretreatments on effective destruction of biomass have been discussed.
- Novel green solvent–based IL and DES pretreatment are discussed.
- Mechanistic path of greener ionic liquid pretreatment process has been deliberated.
- Supercritical carbon dioxide explosion (*Sc*–CO_2) has been documented.

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Lignocellulosic biomass conversion via greener pretreatment methods towards biorefinery applications

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