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Integration of deep eutectic solvent in biorefining process of lignocellulosic biomass valorization

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ABSTRACT

Pretreatment is the crucial step in the biorefinery process for the bioconversion of lignocellulosic biomass to value-added products. Among various chemical pretreatment methods, deep eutectic solvents (DESs) are novel green solvents to effectively reduce the recalcitrant nature of the biomass that result in an increase in the sugar and product yields after the enzymatic saccharification and fermentation process. This review summarizes the properties, mechanisms, applications and parameters of various types of DESs to improve the delignification from the lignocellulosic biomass and fractionation process. In addition, different integrated methods related to DES pretreatment used in recent studies are also discussed in this paper. Even though this strategy is in the infant stage, further research is required to meet the challenges and increase the efficiency of the process. Moreover, such an approach is desirable to ensure the extensive utilization of biomass for developing sustainable products by mitigating global energy crises.

1. Introduction

Lignocellulosic biomass (LCB) plays a significant role in energy sustainability in three significant areas: environment, economy and society. Through the biorefinery process, LCB is converted into both environmentally and economically value-added products (Gundupalli and Sriariyanun, 2022). Biorefinery is a principal component in the structure of the arising bioeconomy because the wide range of biomass offers extraordinary scope for a boundless item portfolio to fulfill the various necessities of society (Hingsamer and Jungmeier, 2019). Earlier, the rise in the cost of crude oil made researchers develop an alternative solution to replace petroleum refining products (Cheng et al., 2020). At present, this biorefining process helps to develop various bioproducts for other industries that are classified as a platform system (product from C_3-C_6 sugars, lignin derivatives, pyrolytic liquids and syngas), end product system (products such as biofuels, additives, chemicals, materials and bioplastics), feedstock system (product from various biomass residues) and process system (product from various reactions) (Takkellapati et al., 2018; Task42, 2022).

The biorefinery process for LCB mainly consists of three steps namely pretreatment, saccharification and fermentation to produce the final product. LCB includes agricultural crop waste, forest residues, and municipal solid wastes that are mainly composed of cellulose (35–50 %), hemicellulose (20–35 %), lignin (5–30 %) and other substances (1–10 %) where the composition range differs in each type of biomass (Chandel et al., 2018; Divya et al., 2015). Both physical (crystallinity, particle size, accessible surface area, and pore volume) and chemical (composition, degree of polymerization, presence of hydroxyl and acetyl groups) properties of LCB contribute to its recalcitrant nature that hinders the production of value-added products (Zoghlami and Paës, 2019). The two significant tasks in biomass conversion are breaking the intact structure of LCB to release the fermentable sugars, which can further be converted into desired bioproducts by fermentation (Bhatia et al., 2020).

Pretreatment of LCB is the initial, most significant rate-limiting and challenging step involved in the conversion of biomass that contributes to 40–60 % total cost of the overall process because it is responsible for releasing the simple compounds required for saccharification (Haldar and Purkait, 2021). During the pretreatment process, the biomass

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undergoes various reactions (degradation and depolymerization) that result in the breakage of intermolecular and intramolecular bonds between cellulose, hemicellulose and lignin and subsequently lead to the improved accessibility of hydrolytic enzymes to the carbohydrates present in the biomass. Thus, it offers maximum sugar utilization and improves the end product yields (Kassaye et al., 2017; Behera et al., 2014). This process is categorized into four major types, such as physical, chemical, physicochemical and biological methods. The efficiency of the pretreatment is determined by the complexity of the selected biomass, formation of inhibitors, yield of bioproducts, energy consumption, economic feasibility and environmental impact (Xu et al., 2016a, 2016b). Hence, efficient pretreatment is inevitable to overcome the physical and chemical barriers of LCB during hydrolysis.

Among the aforementioned pretreatment methods, chemical pretreatment (acid, alkaline, ionic liquids and Deep Eutectic Solvents) is widely used practice because it can alter the structural components of LCB in an uncomplicated and reproducible way to promote lignocellulose disintegration (Galbe and Wallberg, 2019; Jose et al., 2022). However, its application may cause many drawbacks including corrosion, high cost and environmental impacts, such as air and water pollution due to chemicals (Rastogi and Shrivastava, 2017). Another drawback of the processing of LCB is the formation of undesired inhibitors during pretreatment that hinders the metabolic activity of microorganisms (e.g.: yeast metabolism) which causes a negative impact on the effective bioconversion of lignocellulosic hydrolysate to the final product at the time of fermentation processes. In spite of that, the requirement for detoxication procedures results in material losses, affecting the reduction of saccharides in the fermentation medium. As a result, the cost of converting lignocellulose into ethanol and other products with a higher added value may increase (Kordala et al., 2021). Thus, it is required to select a suitable chemical for pretreatment, which is practically environmentally, socially and economically favorable. Among all chemical methods, deep eutectic solvent (DES), which possesses characteristics similar to ionic liquids (ILs), gains much attention globally and is considered a green solvent with many advantages (Wang and Lee, 2021). In light of this, the current review aims to explore the efficacy of the DES pretreatment method, where more focus has been given to its properties, mechanisms, and the parameters that affect the yield of the final product. In addition, the recent research findings of combined studies are also addressed. Moreover, the challenges and future outlooks of the pretreatment of LCB are outlined in this review paper.

2. Overview of DES pretreatment method

DES is a solvent obtained by combining two or more chemical components of quaternary ammonium salts: hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) like amides, carboxylic acids, and polyols in a specific molar ratio. Continuous stirring during the preparation of DES causes a rearrangement of strong hydrogen bond interaction resulting to obtain a liquid solvent mixture, which has a lower melting point and can crystallize compared to those of parent compounds (Kalhor and Ghandi, 2019; Liu et al., 2017). The hemicellulose-lignin complex in LCB is stabilized by the supramolecular H-bond, which makes it easier to break the covalent link. In this manner, it is also conceivable to reorder the various components under moderate circumstances without creating any potential inhibitors to the subsequent depolymerization of cellulose to yield glucose (Zulkefli et al., 2017). This green solvent was first synthesized and reported in 2003 to have both the characteristics of ILs and organic solvents (Abbott et al., 2003). In the beginning, DES was used in mineral processing, analytics, electrochemistry, extractions, catalysis, and for preparing media or templates (Lyu et al., 2019). Since 2012 onwards, DES is widely used as a solvent in LCB pretreatment in biorefinery processes (Francisco et al., 2012).

2.1. Characteristics and mechanism of DES

On one hand, DES has some similar properties to ILs, such as being non-flammable, non-volatile, recyclable and eco-friendly, with low vapor pressure, melting point, thermal stability and air stability. On another hand, it differs from ILs due to its high solubility of lignin when compared with cellulose and hemicellulose. Additionally, other properties, including low cost compared to ILs, high purity, less toxic, biodegradable, and easy preparation, add the advantages to DES as a promising solvent for the chemical pretreatment of LCB. The employing DESs as a substitute for an IL is more efficient and produced greater yields than the IL in the enzymatic synthesis of biodiesel from waste oil. The yield obtained when using 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6] was 63 % lower, after 4 h of a reaction, than that of ChCl: Glycerol (1:2) DES, and it climbed to 71.4 % when ternary DES with 4 % water was utilized (Merza et al., 2018).

DES mainly breaks the ether bonds without affecting the bonds between the carbon atoms, leading to delignification during pretreatment. In such a way, it helps to valorize the lignin by producing homogenous lignin nanoparticles, thus it is recognized as the significant mechanism of DES (Xu et al., 2020a, 2020b). The DES has a lower melting point than the individual components due to the charge delocalization promoted by forming a hydrogen bond (H-bond) between HBA and HBD (Fig. 1). A stronger H-bond results in a greater decrease in melting point (Kalhor and Ghandi, 2019).

DES pretreatment is primarily focused on removing non-crystalline complexes, such as hemicellulose and lignin, therefore the biomass crystallinity index rate increased due to the presence of high cellulose content in the sample after the pretreatment. This is affected based on the molarity of DES used in the experiment. The study on corncob by Zhang et al. (2016) identified a suitable molar ratio for DES (ChCl: Lactic acid) as 1:2 at 90 °C for 24 h, where high lignin was removed and high crystallinity index was obtained (Zhang et al., 2016). The same type of biomass with different HBD (ChCl: Imidazole) with a molar ratio of 3:7 reached high values of the crystallinity index ranging from 40.08 to 49.22 % when the temperature was raised from 115 to 150 °C (Procentese et al., 2015). Therefore, biomass with higher crystallinity needs severe temperature for DES pretreatment with a stronger ability to break down the constituents of raw material for easy accessibility of hydrolytic enzymes. Another factor that affects the pretreatment efficiency is the particle size of the raw material. The lower the particle size, the higher will be the pretreatment efficiency. During DES pretreatment, the appropriated range of particle size for most biomass is probably taken as 0.5–5 mm (Xu et al., 2020a, 2020b).

The efficiency of the DES depends on the type of raw material. Wide varieties of biomass were tested for DES pretreatment, including wastes from agriculture (vegetables and fruits), forestry and bioenergy crops (Bhatia et al., 2020). The recalcitrant network structure of cellulose (crystalline and amorphous), hemicellulose and lignin (syringyl, hydroxyphenyl and guaiacyl subunits) present in the lignocellulosic biomass negatively affects the enzymatic saccharification after pretreatment. Mostly, the amorphous structure can be easily hydrolyzed, but the presence of lignin, a complex aromatic biopolymer, is difficult to remove and inhibits the enzymatic activity during saccharification (Takada et al., 2020; Yoo et al., 2020). Therefore, the pretreatment efficiency is determined based on the polysaccharide recovery yield, dissociation degree of cellulose and hemicellulose, and lignin removal rate (Wang et al., 2015). Usually, during the pretreatment process, the dissociation of aryl ether bonds and ether bonds of lignin and hemicellulose occurs. In the case of DES pretreatment, the cellulose dissociation efficiency is low, and the solubility of hemicellulose in DES is higher than cellulose. Additionally, high lignin removal was also reported (Kumar et al., 2016; Suopajärvi et al., 2020). The morphological changes of cellulose, hemicellulose and lignin are influenced by the DES pretreatment (Liu et al., 2019a, 2019b; Lou et al., 2019; Song et al., 2019).

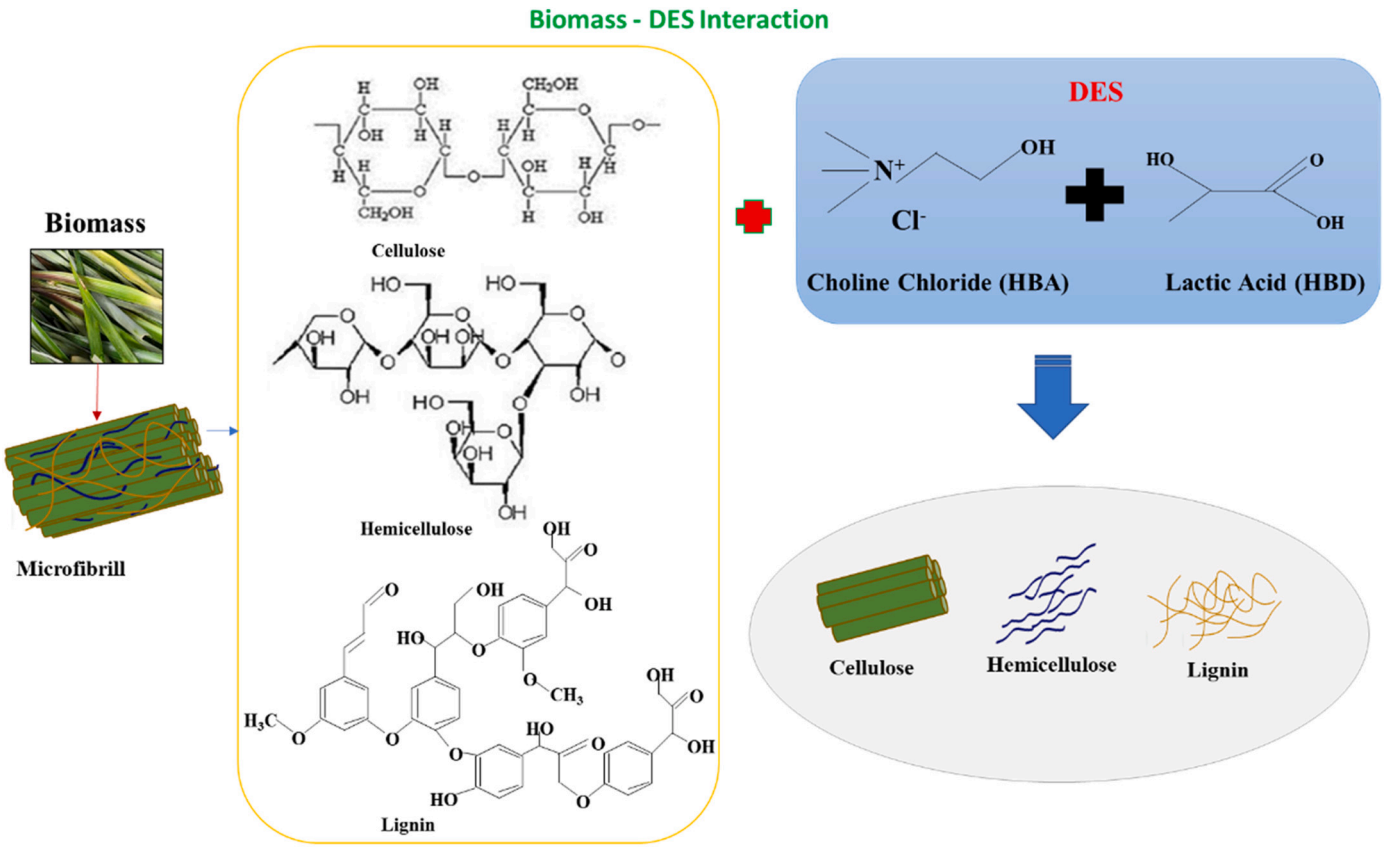

Fig. 1. Elucidation of biomass-DES interaction in the DES pretreatment.

2.2. Classification of DES

The nature of the DES depends on the characteristics of HBD and HBA and their molar ratios and combinations. Choline chloride (ChCl) is the most common HBA used for DES synthesis as it is biodegradable, low price, non-toxic and has high productivity (Chen et al., 2018b). In addition, ChCl could stabilize the protein components and helps enzyme accessibility during saccharification (Galbe and Wallberg, 2019). Other HBAs, such as ethylene glycol (EG), ethylammonium chloride (EAC), ethylamine chloride (EaCl), benzyltrimethylammonium chloride (BTMAC), triethylbenzyl ammonium chloride (TEBAC), 2,3-dihydroxy-propyl-1-triethylammonium chloride or $[C_9H_{22}N^+O_2]Cl^-$ (DPTAC), alanine (AL) and betaine (BA) and proline, have been also selected for DES synthesis (Panakkal et al., 2021).

HBD has been demonstrated to be an important component to determine the property of DES rather than HBA. HBDs differ from each other by their chemical structures and arrangements, such as chain length, differences in functional groups and several functional groups. Hence, the acidity and polarity of synthesized DES are influenced by these factors. The carbohydrate-based HBD is not recommended for fractionating LCB due to its low dissolution ability (Haldar and Purkait, 2021; Tan et al., 2020). Acid, base and polyalcohol-based HBDs have been demonstrated to be applied for biomass conversion. Table 1 contains studies done using different types of HBD, combinations with HBA and the parameters used to obtain optimal sugar yield and lignin removal.

Commonly used DES with acid-based HBD includes carboxylic acids, such as acetic acid, formic acid (FA), glycolic acid, oxalic acid (OA), lactic acid (LA), glutaric acid, malonic acid, levulinic acid, malic acid (Mal), p-coumaric acid (PCA), citric acid, tartaric acid, proline, butanoic acid, maleic acid, propanoic acid, succinic acid, and chloropropionic acid. Ji et al., studied the effect of seven types of acidic DESs on sugarcane bagasse for the production of 5-Hydroxymethylfurfural and found that carboxylic acid DES is a promising solvent for the biomass fractionation and conversion (Ji et al., 2021). The effectiveness of the pretreatment is often influenced by the hydrocarbon chain length and the functional group of HBD. For instance, monocarboxylic acid could remove lignin comparatively better than dicarboxylic acids (Teles et al., 2017). Likewise, lactic acid and levulinic acid have lower delignification efficiency than malic and glutaric acid. Also, lignin solubility could be high for DES with monocarboxylic acid and shorter alkyl chain length than dicarboxylic acid DES (Suopajärvi et al., 2020). In contrast, high-polarity HBDs will have a lower delignification rate (Haraźna et al., 2019).

One category of HBD is the polyol alcohol that includes EG, glycerol (Gly), butanediol, 4-hydroxybenzyl alcohol, pyrocatechol, xylitol, 1,2-propanediol, and 1,3-propanediol. Polyol HBD shows a differential lignin removal rate based on the molecular and functional group arrangement parameters, such as temperature, and reaction duration, though it require more severe condition than the acid-based HBDs (Teles et al., 2017). The hydrophobic nature of polyol-based DES promotes biomass fractionation. Using glycerol as HBD could reduce the corrosion effect to the process instruments (Wang and Lee, 2021). Even though polyols enhance the saccharification due to the absence of acidity, they result in a low rate of xylan and lignin removal. Therefore, combining the acid and polyol HBD in the pretreatment will enhance the removal rate of both xylan and lignin.

Other categories of alkaline HBD are the amines or amides (urea (U), acetamide, trifluoro acetamide (TFA), monoethanolamine (MEA), imidazole (IM), diethanolamine, methyldiethanolamine and formamide), which are used mostly for the pretreatment process. Therefore, the mechanism involved in the delignification is the deprotonation of phenolic hydroxyl groups. It should be noted that both polyols and amines/amides also required severe conditions for the pretreatment

Table 1
Various combinations of HBA and HBD to form DES for lignocellulose pretreatment.

Types of DES		Biomass	Molar ratio	Parameters			Sugar yield (%)	Lignin removal (%)	Ref
HBA	HBD			Temp	Time	Solid loading			
ChCl	**Carboxylic acids**								
	Formic acid (FA)	Eucalyptus	1:2	120 °C	90 min	100 g	90.3	80.7	(Zhang et al., 2022a, 2022b)
	Acetic acid	Bambara groundnut haulm	1:2	100 °C	3 h	3 g	79.44	57.63	(Okuofu et al., 2022)
	Glycolic acid	Akebia herbal residues	1:6	120 °C	8 h	10 g	71.5	60	(Yu et al., 2018)
	Oxalic acid (OA)	Bamboo shoot shell	1:2	120 °C	1.5 h	1 g	74.1	47.8	(Dai et al., 2017)
	Lactic acid (LA)	Corn stover	1:2	130 °C	2 h	10 g	82.70	61.93	(Liang et al., 2021)
	Glutaric acid	Corncob	1:1	90 °C	24 h	0.3 g	40.7	34.3	(Zhang et al., 2016)
	Malonic acid	Corncob	1:1	90 °C	24 h	0.3 g	61.5	56.5	(Zhang et al., 2016)
	Malic acid (Mal)	Corncob	1:1	90 °C	24 h	0.3 g	37.4	22.4	(Zhang et al., 2016)
	Levulinic acid	Moso bamboo	1:2	80 °C	2 h	3 g	79.07	28.9	(Ling et al., 2020)
	p-Coumaric acid (PCA)	Switchgrass	1:1	160 °C	3 h	5 g	47.9	60.8	(Kim et al., 2018)
	Citric acid	Oil palm empty fruit bunch (OPEFB)	1:1	120 °C	8 h	10 g	58	23	(Tan et al., 2019)
	Butanoic acid	OPEFB	1:2	120 °C	8 h	10 g	50	15	(Tan et al., 2019)
	Maleic acid	OPEFB	1:1	120 °C	8 h	10 g	64	21	(Tan et al., 2019)
	Propanoic acid	OPEFB	1:2	120 °C	8 h	10 g	54	15	(Tan et al., 2019)
	Chloropropionic acid	Rice straw	1:1	120 °C	6 h	300 g	82.5	31.95	(Hou et al., 2018)
	Polyols and alcohols								
	Ethylene glycol (EG)	Corncob	1:2	90 °C	24 h	0.3 g	85.3	87.6	(Zhang et al., 2016)
	Glycerol (Gly)	Corncob	1:2	90 °C	24 h	0.3 g	96.4	71.3	(Zhang et al., 2016)
	Butanediol, 4-hydroxybenzyl alcohol	Wheat straw	1:2	120 °C	2 h	0.3 g	85	54	(Guo et al., 2018)
	Catechol	Switchgrass	1:1	160 °C	3 h	5 g	53	49	(Kim et al., 2018)
	Xylitol	Bamboo	1:2	120 °C	3 h	3 g	96.08	80.75	(Wang et al., 2022)
	1,2-Propanediol	Rice straw	1:1	120 °C	3 h	300 mg	36.3	19	(Hou et al., 2018)
	1,3-Propanediol	Rice straw	1:1	120 °C	3 h	300 mg	41.8	19	(Hou et al., 2018)
	Amines or amides								
	Urea (U)	Rice straw	1:2	130 °C	8 h	10 g	0.78	44.74	(Pan et al., 2017)
	Acetamide	Wheat straw	1:2	90 °C	12 h	5 g	97.6	3.4	(Zhao et al., 2018)
	Monoethanolamine (MEA)	Wheat straw	1:6	90 °C	12 h	5 g	92.4	81	(Zhao et al., 2018)
	Diethanolamine	Wheat straw	1:8	90 °C	12 h	5 g	98	73.5	(Zhao et al., 2018)
	Methyldiethanolamine	Wheat straw	1:10	90 °C	12 h	5 g	98.6	44.6	(Zhao et al., 2018)
	Formamide	Rice straw	1:1	120 °C	6 h	300 mg	41.4	15.03	(Hou et al., 2018)
	Imidazole (IM)	Corncob	3:7	150 °C	15 h	6.25	46.7	88	(Procentese et al., 2015)
	Other HBDs								
	Boric acid (BA)	Microcrystalline cellulose	5:2	80 °C	24 h	NA	50 %	NA	(Wahlström et al., 2016)
	D-Glucose	OPEFB	1:1	120 °C	8 h	10 g	30	18	(Tan et al., 2018)
	Vanillin (Van)	Switchgrass	1:2	160 °C	3 h	5 g	51	52.5	(Kim et al., 2018)
	Guanidine HCl (GH)	Rice straw	1:1	120 °C	6 h	300 mg	37.4	17.32	(Hou et al., 2018)
EAC	EG	Oil palm trunk	1:2	100 °C	48 h	5 g	74	42	(Zulkefli et al., 2017)
EaCl	LA	Corncob	1:1	150 °C	0.5 h	10 g	98	71.5	(Xu et al., 2020c)
BTMAC	LA	Corncob	1:2	140 °C	2 h		94	63.4	(Guo et al., 2019)
TEBAC	LA	Wheat straw	1:9	100 °C	10 h	2 g	89.06	75.6	(Liu et al., 2019a, 2019b)
BA	LA	Xylose residues	1:2	120 °C	2 h	1 g	89.8	81.6	(Guo et al., 2018)

(Ong et al., 2019). Other HBDs are boric acid (BA), monosaccharides (D-glucose & D-fructose (Fru)), vanillin (Van), p-toluenesulfonic acid monohydrate, and guanidine hydrochloride (GH). When comparing all types of aforementioned HBDs, acid-based HBD has a better performance in delignification during DES pretreatment. The high polarity and high acidity of DES add the advantage to the delignification of biomass (Panakkal et al., 2022).

3. Factors affecting the efficiency of DES pretreatment

Similar to other pretreatment methods, the efficiency of DES pretreatment also depends on certain parameters, such as the molar ratio of HBA and HBD, temperature, reaction duration and solid-liquid ratio. In this paper, the effects of all pretreatment parameters will be discussed. It is also found that optimizing these parameters is essential in the pretreatment of any biomass to enhance the yield of the final product.

3.1. The molar ratio of HBA and HBD

Some properties of DES, such as freezing point, melting point, viscosity, density and ionic conductivity depend on the nature and molar ratio of HBA and HBD (Sharma et al., 2022). Zhou et al. studied the mechanism behind the DES having the melting point lower than 150 °C due to certain interactions, for instance, H-bonding, and charge delocalization from the halide ion of HBA to the HBD or Van der Waals force of attraction between the DES mixture (Zhou et al., 2022). The melting point is related to hydrogen bonds between HBD and HBA. The lower hydrogen bonds and higher melting points were the features of the DES mixture. Conversely, DES having low viscosity has an advantage over the industrial application, as it helps for better mixing and increased interfacial area for converting the LCB. The molar ratio between HBA and HBD determines the viscosity of the DES mixture. The combinations of DES using a molar ratio 1:2 of ChCl: EG, ChCl: Gly and ChCl: U showed low viscosities of 37 mPa second (mPa·s) at 25 °C, 80 mPa·s at 50 °C and 120 mPa·s at 50 °C, respectively (el Achkar et al., 2021). Furthermore,

the molar ratio of HBA and HBD can change the density of the DES mixture. Removal of lignin efficiently occurs when the density of the DES mixture is finely tuned. Density increases when the molar ratio of HBD increases, but it drops at a high molar ratio of HBA (Basaiahgari et al., 2017; Shafie et al., 2019). Likewise, ionic conductivity also depends on the molar ratio of HBA and HBD, which can be altered by increasing or decreasing the salt concentration (el Achkar et al., 2021).

Similarly, the efficiencies of DESs for lignin removal also depend on the nature and molar ratio of HBA and HBD. Once the molar ratio of ChCl: LA rose from 1:2 to 1:9, solid recovery dropped and lignin removal increased from 33 to 76 %. Also, glucose yield obtained from pretreated rice straw increased 36–40.5 % under the pretreatment condition (with solid loading 5 % (*w/v*) and a temperature of 121 °C for 1 h) (Kumar et al., 2018). A similar trend was observed by several researchers who varied the molar ratio of LA to ChCl, while treating different biomass, such as corncob, wheat straw, empty fruit bunches, Moso bamboo and hardwood willow. It is also reported that lignin was removed considerably when the molar ratio of ChCl to LA was increased from 1:1 to 1:15 (Jablonský et al., 2015; Li et al., 2017; Liu et al., 2019a, 2019b; Tan et al., 2019; Zhang et al., 2016). Furthermore, it enhanced cellulose digestibility and final reducing sugar yield (Li et al., 2018). Therefore, the molar ratio of HBA and HBD greatly influences the rate of delignification in the fractionation of biomass, subsequently, increasing the efficiency of the pretreatment.

3.2. Temperature

Temperature plays a significant role in improving DES pretreatment efficiency. Mostly in DES pretreatment, the temperature range starts from 60 to 200 °C. The study of acidic DES on sugarcane bagasse (SCB) by Ji et al., found that the pretreatment efficiency of ChCl: LA was influenced by changing the temperature range from 80 °C to 110 °C. The yield of glucose was reduced, formic acid was increased and no noticeable change in the yields of furfural and β-D-glucose was observed. It is suggested to maintain the temperature at 110 °C to valorize 5-hydroxymethylfurfural (5-HMF). Since, at 110 °C, the internal structural components of the biomass disintegrated quickly, the amount of sugar rose quickly, and isomerization and dehydration of glucose and fructose continued to occur and ultimately increased the yield of 5-HMF (Ji et al., 2021).

High temperature sometimes negatively correlates with both glucose and xylose recovery rates. This is due to the breakdown of polysaccharides during enzymatic saccharification results in the loss of carbohydrates. Moreover, at high temperature, the DES loses thermal stability (Chen et al., 2018a). Even if lignin and hemicellulose are removed at high rates at high pretreatment temperatures, an appropriate temperature should be carefully chosen while taking into account certain benefits like low toxicity, cheap cost, and environmental friendliness. At mild temperatures, using lactic acid or glycerol as the HBD, Provost et al. examined the lignin extraction yields from pretreated softwood or grain biomass at 60 and 80 °C. The lignin extraction yield for both biomasses under ChCl: LA pretreatment increased as the temperature rose from 60 °C to 80 °C. For softwood chips powder and brewer's spent grains, lignin extraction yields of 56.7 % and 34.5 % were achieved at 60 °C, and these values improved to 77.7 % and 39.3 % at 80 °C respectively (Provost et al., 2022).

3.3. Solid-liquid ratio

The solid-liquid ratio is the ratio of the biomass and DES that was taken for the pretreatment. This is a key parameter in increasing the efficiency of the pretreatment by controlling biomass dissolution and DES penetration (Xu et al., 2020a, 2020b). Ji et al. studied the biomass sugarcane bagasse (SCB) and ChCl: LA ratio from 1:2.5 to 1:10. The yield of 5-HMF increased from 7.52 to 21.23 mol% and glucose yield rose from 20.22 to 29.10 mol%. Further increase in this ratio resulted in the decrease of the product (5-HMF) and glucose yield (20.06 mol%). The penetration and disintegration of the SCB by the DES may be a major factor in this phenomenon. The SCB could not be completely contacted by the DES at a lower concentration in the reaction system, which reduced the force of the DES acting on the SCB and slowed down the dissociation of the SCB structure. The yields of sugar and 5-HMF were low because the reaction system did not have enough acidic sites to encourage the hydrolysis of cellulose and hemicellulose (Ji et al., 2021). In contrast, the SCB was solubilized in DES and its structure was disintegrated when the amount of DES in the reaction was large (Alexander et al., 2020). Hence, this study suggested that a suitable solid-liquid ratio should be selected to enhance the delignification and saccharification of cellulose and hemicellulose to increase the yield of final product.

3.4. Reaction time

Another factor that affects lignin removal and prevents carbohydrate dehydration is the prolonged reaction time ranging from 0.5 h to 24 h. Pretreatment of lettuce with ChCl: Gly (1:2) at 150 °C for different times at 3 h, 6 h, and 16 h was tested and the optimal yields of glucose and xylose were obtained at 94.9 % and 75.0 %, respectively, from enzymatic hydrolysis after pretreatment with ChCl: Gly at 16 h (Procentese et al., 2017). Similarly, in another study by Xu et al. (2018), the sugar yield (84 %) was achieved when the pretreatment time duration was increased from 2 h to 8 h using DES ChCl: Gly at 160 °C (Xu et al., 2018). Although, prolonged pretreatment time helps the cellulose fiber to be swollen, consequently, increasing the surface area and thus increasing the accessibility of hydrolytic enzymes to substrate during saccharification (Li et al., 2014). Normally, a longer duration of pretreatment during pilot-scale production in industries could cause lower productivity and high energy consumption due to the formation of toxic products and sugar degradation.

3.5. Combined pretreatment factors

The recalcitrant nature of the LCB hinders the components from releasing the sugar monomers or oligomers during enzymatic saccharification. For the valorization of biomass to value-added bioproduct, it is essential to undergo pretreatment to alter the structure. Maintaining the ideal pretreatment condition, which includes the effect of the aforementioned variables (molar ratio, temperature, reaction time and solid-liquid ratio) are crucial for improving the efficacy of DES pretreatment (Gundupalli et al., 2022). Hence, these factors play a significant role in the pretreatment process to react with the components of the biomass (cellulose, hemicellulose and lignin) sufficiently. Extreme pretreatment conditions often lead to the formation of inhibitors and the degradation of the products. Thus, optimization of these parameters is very much essential for achieving better treatment efficiency.

Some biomass requires high temperature, less solid loading, and low duration time to produce maximum yield. In a few cases, the pretreatment is suggested to conduct at a low temperature, with a high solid loading rate and long reaction time. Therefore, all these parameters are interconnected and require further research to identify optimum conditions for each biomass. The cellulose, hemicellulose and lignin contents could also vary for each LCB and properties. For example, wheat straw provides better results at low pretreatment severity as it has low density, short cell length, and a thin cell body (Lou et al., 2019). There are a few numbers of software and techniques that are widely used like Response Surface Methodology (RSM) tool to study the operating conditions required for biomass pretreatment (Panakkal et al., 2022). RSM helps to identify the optimum conditions with fewer experiments compared to conventional optimization methods and also facilitates the identification of interactions between various pretreatment parameters. It helps to analyze the parameters to improve and formulates a better outcome (Sablania and Bosco, 2018). Many researchers use computational methods like ab Initio Methods, molecular dynamic simulation,

quantum calculations, or machine learning for the study of DES biomass interactions to finalize the optimum conditions (Ci et al., 2020; Hansen et al., 2021; Kalhor and Ghandi, 2019; Kim et al., 2020; Xu et al., 2020a, 2020b). Using modeling studies could save labor costs and increase research efficiency. The main challenge faced by the researchers is the investigation of the reaction mechanism of DES due to the complexity and heterogeneity of biomass.

4. DES-derived streams

4.1. Cellulose-rich stream

In LCB, cellulose is arranged in the form of a fibril bundle. These fibrils contain glucose units arranged linearly and are joined together by β(1–4) glycosidic bonds to form microfibrils. Cellulose microfibril has a compact and rigid structure with a strong hydrogen bond between and within molecules (Fig. 1). It occurs in a crystalline state (with an ordered structure) and is converted to an amorphous condition (with a disordered structure) by an effective pretreatment method (Sunday and Mathew, 2019; Zoghlami and Paës, 2019). During DES pretreatment, the HBA component weakens these intermolecular and intramolecular hydrogen bond and promotes cellulose dissolution based on the hydrogen bond basicity (β) of the DES (Chen and Mu, 2019). This β bonding property of DES is affected by the presence of anions such as Cl^-, OAc^-, $HCOO^-$, $(MeO)_2PO_2^-$, and others (Wang et al., 2020a, 2020b). Comparatively, DES dissolves cellulose with less efficiency than ILs because ILs attack biomass with their anions and cations. Whereas, DESs function in the disintegration process by rearrangements of hydrogen bond associated with cellulose. One method to increase the solubility of cellulose is by combining DES with ILs. For instance, the study was done by comparing the cellulose dissociation with the mixture of alkyltriethylammonium chloride: OA and ChCl: OA. It was found that alkyltriethylammonium chloride: OA obtained higher solubility of cellulose (6.48 %) than ChCl: OA pretreatment (Ren et al., 2016). Valorization of cellulose after DES pretreatment results in the formation of primary and secondary bioproducts like nanocellulose, nanomaterials, aerogels, composite materials, carbon dots, paper, pulp, textiles and fibers. DES is used to produce various value-added products as listed in Table 2.

4.2. Hemicellulose-rich stream

Hemicellulose is an amorphous component of LCB that is composed of linear (hexoses and pentoses) and branched (uronic acids) chains of heteropolysaccharides. It coats the cellulose fibrils through weak hydrogen bonds and Van der Waals force. Depending on the lignocellulose species, there are differences in the hemicellulose content and structure, the length and type of main chain, and the distribution and type of side chains (Lu et al., 2021). It is easier to remove hemicellulose from the recalcitrant structure of lignocellulose biomass during pretreatment compared with cellulose (Frassoldati and Ranzi, 2019; Huang et al., 2021). During DES pretreatment, xylose can be removed due to the formation of an intermolecular hydrogen bond between the DES and hemicellulose by breaking the intermolecular hydrogen bond between hemicellulose and lignin and cellulose. Temperature effects were studied using acidified, aqueous ChCl: Gly on the fractionation of switchgrass and found that xylose removal was increased by 18.1 % when the temperature increased from 110 to 120 °C for 1 h (Chen et al., 2018b). However, the high viscosity of pure DES sometimes hinders the dissolution of xylan. Therefore, aqueous DES pretreatment (66.7 wt% water and 50 % ChCl: U) is found suitable to increase the xylan removal (328.23 $g{\cdot}L^{-1}$) in hardwood (Morais et al., 2018). Hemicellulose extraction is used in the biorefinery process to obtain specific products, such as bioethanol, biodiesel, biohydrogen, and furfurals (Table 2).

Table 2
DES used for the valorization of LCB.

Biomass	DES types	Bioproduct	References
Softwood	ChCl: OA	Cellulose nanocrystals	(Laitinen et al., 2017a)
Raw ramie fibers	ChCl: OA	Cellulose nanomaterials	(Yu et al., 2020)
Cellulose pulp	ChCl: U	Aerogels	(Laitinen et al., 2017b)
Corn stover, peanut shell powder, sugarcane bagasse	ChCl: Gly	Biocomposite	(Fatima Haq et al., 2022)
Tea residue	ChCl: U	Carbon dots	(Huang et al., 2022)
Eucalyptus wood chips	ChCl: LA	Pulp	(Chen et al., 2021a, 2021b)
Saccharum spontaneum	ChCl: Gly and Ca $(OH)_2$	Bioethanol	(Vaid et al., 2021)
Yarrowia lipolytica	ChCl: Glucose	Biodiesel	(He et al., 2022)
Corncob	ChCl: Ethanolamine	Biohydrogen	(Jing et al., 2022)
Switchgrass	ChCl: EG and acetone	Furfural	(Chen and Wan, 2019)
Poplar wood	ChCl: OA	Bioplastic	(Xia et al., 2021)
Boehmeria nivea (L.) Gaud	ChCl: U	Biochar	(Ye et al., 2021)
Sorghum	ChCl: LA	Phenolic compounds	(Das et al., 2018)
Wheat straw	ChCl: Zinc chloride	Resin	(Hong et al., 2016)
Vanilla pods	LA: Propanediol, LA: Fru	Vanillin	(González et al., 2018)
Corn stover	ChCl: EG, ChCl: OA, ChCl: FA	Films	(Zhang et al., 2022a, 2022b)

4.3. Lignin-rich stream

The major challenge faced in the biorefinery process is the dissolution of the lignin present in the LCB due to its highly recalcitrant property. Lignin is a rigid chemical structure that holds cellulose and hemicellulose together and it is composed of phenyl propane alcohol units (coumaryl, coniferyl, and sinapyl) with ether bonds. It contributes strongly to the recalcitrant nature of LCB and it has a natural function to protect plants from pathogen attacks (Lourenço and Pereira, 2018). Among different types of pretreatment methods, DES allows effective delignification that enhances the overall production rate of biorefinery products (Sharma et al., 2022). Among various types of HBAs, ChCl-derived DES was found to be more efficient in removing lignin during pretreatment due to the presence of chloride ions that helps to react with cellulose and hemicellulose structures. Likewise, acidic HBDs show a significant amount of lignin removal from the lignin-carbohydrates complex (Chen et al., 2020). Li et al., investigated lignin removal efficiencies by using seven types of DESs on sugarcane bagasse and found a higher solubility rate for lignin when treated with acidic DES than basic DES (Li et al., 2021). Pretreatment by using BTMAC/LA mixture removed 63.4 % lignin, which contains guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) structures from biomass (corncob) (Guo et al., 2019; Li et al., 2021). The content of G-type lignin was higher when sunflower seed shells were treated by the acetic acid method. Whereas, S-type lignin was degraded when treated with a low ratio of ChCl: Gly indicating that DES pretreatment helps to enhance the lignin reactivity (Gong et al., 2017). Hence, this evidence proves the efficiency of DES pretreatment in delignification. Many products derived from lignin can be obtained, such as bioplastics, phenolic compounds, resins, vanillin, dye dispersants and aromatics.

Over 70 % of the delignification and 90 % of the enzymatic saccharification are produced by the several various DES systems that have been studied up to this point. However, even in moderate

circumstances, the structural integrity of the recovered lignin in published publications is typically drastically changed and challenging to use further. Utilizing reactive lignin appears to be crucial to the success of lignin-first DES pretreatment (Huang et al., 2020a, 2020b; Shen et al., 2020). Cheng et al. explored the pretreatment of bamboo using a diol-based DES, attaining over 80 % lignin removal while keeping nearly all glucans to avoid undesirable lignin condensation in typical DES pretreatment. Significantly, the regenerated lignin has a very high β-O-4 percentage (31.82 %–59.19 %), which is advantageous for the downstream process of lignin (Cheng et al., 2022). To improve the value of DES lignin and benefit the processing of the entire DES-based biorefinery, the integrity of the lignin must be protected during DES pretreatment.

5. Future outlook and challenges

5.1. Combinatorial study of DES with other pretreatment methods

Recently, researchers emphasized combining DES pretreatment methods with other physical, chemical, physio-chemical and biological methods to increase the efficiency of the process. Such studies include microwave, ultrasound, acids, alkalis, organosolv, hydrothermal, surfactant, and biological methods. Combining physical methods, such as microwave irradiation and ultrasound with DES pretreatment increase the efficiency and accelerate the reaction rate (Roy et al., 2020). Chen and Wan studied DES pretreatment integrated with microwave technology to pretreat three types of LCB (switchgrass, corn stover, miscanthus). A significant increase of 74 % glucose yield was found when they used ChCl: LA in the molar ratio 1:2 combined with microwave irradiation for 45 s. The biomass structure was disintegrated by the microwave electromagnetic field, primarily due to the molecular collision brought by dielectric polarization. DES molecular polarity was also raised by microwave radiation, which made the pretreatment more effective (Chen and Wan, 2018). Another method that gained attention is the combination of ultrasound with DES, which improves delignification by changing the structure and morphology of biomass (making cavitation), resulting in the dissolution and fractionation of the LCB components. Lee et al., investigated the synergistic effect of ultrasonication with DES (ChCl: LA, ChCl: U and ChCl: Gly) on OPEFB. Reducing sugar yield increased (36.7 %) for ChCl: LA pretreated sample when treated for 15 min at sonication power 60 % (210 W) and temperature 50 °C, followed by ChCl: U (35.8 %) and ChCl: Gly (35.3 %), respectively (Lee et al., 2021). In another study, ChCl: U (1:2) reduced lignin to 14.1 % at 30 min ultrasonication (Ong et al., 2019). Recent studies have focused on the hydrothermal approach that increases the delignification of hardwood feedstock. Compared with other physical methods, the main advantage of this method is the capability to disintegrate the components of biomass separately with a maximum yield of bioproducts (Gundupalli et al., 2022; Sharma et al., 2022; Wang and Lee, 2021). Table 3 provided a few case studies related to DES pretreatment integrated with other pretreatment methods.

DES pretreatment integrated with other chemical methods includes acids, alkalis, catalysts, and surfactants. The efficiency of Lewis acids, such as $AlCl_3.6H_2O$, $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $ZnCl_2$, and $CuCl_2$ have been studied with ChCl: Gly at a 1:2 molar ratio to develop highly pure and antioxidative lignin. Cellulose hydrolysis showed an increased rate of 99.5 % in hybrid *Pennisetum*. Meanwhile, this combined pretreatment obtained the removal of lignin and hemicelluloses at 78.88 wt% and 93.63 wt%, respectively, due to the synergistic effect of Lewis acid (Wang et al., 2020a, 2020b). The advantage of using surfactant with DES is that it can reduce surface tension. Thus, this result is the deconstruction of biomass structure and increases the surface area, solubility and mass transfer (Sánchez et al., 2022; Vaid et al., 2021). DES pretreatment combined with a surfactant, for instance, Tween 80 with ChCl: OA-EG exhibited high glucan (85.72 %) and xylan (91.05 %) yields from pretreated bamboo because surfactant prevents the attachment of lignin with cellulolytic enzymes (Li et al., 2022).

Another novel strategy was established with the combined DES-biological method using bacterial strain *Pandoraea* species B-6 and ChCl: LA for the pretreatment of rice straw. Bacterial strain enhanced lignin depolymerization by destroying the S unit of lignin and subsequently promoting DES function. This combined method improved the sugar yield by 0.3–1.5 times compared to untreated biomass (Liu et al., 2018). However, further research is required for designing and studying the mechanism in the combined methods with DES to take up the large-scale production of bioproducts in the industrial sector, which could be cost-effective and eco-friendly.

5.2. Cost and energy demand

Pretreatment is the crucial step in the biorefinery process to valorise the bioproduct. Low cost and energy requirements determine the possibility of the pretreatment whether it can be adapted to industrial pilot-scale production and commercialization of bioproducts (Huang et al., 2020a, 2020b). A techno-economic study on the production of bioethanol from rice straw through DES pretreatment was conducted by

Table 3
Few studies related to the combinatorial study of DES with other pretreatment methods.

Biomass	Pretreatment		Operating parameters (biomass loading, temperature & time)	The efficiency of the process	Delignification rate (%)	References
	Combined method	DES (molar ratio)				
Switchgrass, corn stover, miscanthus	Microwave (800 W)	ChCl: LA (1:2)	25–152 °C, 45 s	74 % glucose yield	–	(Chen and Wan, 2018)
Wheat straw	Microwave (360 W)	ChCl: FA (1:3)	10 % (w/v), 8 min	99 % glucose and 85 % xylose yield	27.7	(Isci et al., 2020)
OPEFB	Ultrasonication	ChCl: LA (1:5), ChCl: U (1:2), ChCl: Gly (1:2)	10 % (w/v), 40–60 °C, 50–60 min, 210-350 W	36.7 %, 35.8 %, 35.3 % reducing sugar yield	–	(Lee et al., 2021)
Watermelon rind	Ultrasonication	ChCl: LA (1:6),	0.5 g, 120 °C, 180 min, 180 W	89.80 % fermentation efficiency	43.56	(Fakayode et al., 2021)
Sugarcane bagasse, rice straw, Napier grass	Hydrothermal	ChCl: LA (1:2)	2 g, 130 °C, 95 min, and Hydrothermal: 121 °C, 40 min	90 % glucose yield for all biomasses	65.94 %, 48.73 %, and 54.18 %	(Gundupalli et al., 2022)
Hybrid *Pennisetum*	Lewis acid ($FeCl_3$)	ChCl: Gly	2 g, 60–140 °C, 1-9 h	99.5 % glucose hydrolysis	78.88	(Wang et al., 2020a, 2020b)
Wheat bran	Organic acid (acetic acid)	ChCl: LA (1:8)	2 g, acetic acid (0–20 % (v/v), 140–170 °C, 20–50 min) 130 °C, 90 min.	72.8 % glucose yield	64.6	(Wang et al., 2020a, 2020b)
Dendrocalamus sinicus	Surfactants (Tween 80)	ChCl: OA: EG (1:1:5)	10 g, 110–140 °C, 6 h.	85.72 % glucose and 91.05 % xylose yields	–	(Li et al., 2022)
Rice straw	*Pandoraea* sp. B-6	ChCl: LA (1:5)	1 g, 90–140 °C, 2-8 h	152 % reducing sugar yield	–	(Liu et al., 2018)

Peng et al. It was found that acidic DES showed better economical results in biomass refining. Utilizing low-price DES, such as ChCl-based DES, reduces the process cost. Additionally, high solid-loading pretreatment and combined heat and power positively impacted cost reduction (Peng et al., 2021). A techno-economic study by Kumar et al., showed that bioproducts, such as lignin, xylan, silica and many more from natural DES were necessary for biorefining (Kumar et al., 2020). The lignin obtained during pretreatment can be utilized for further processing (sold or burned), thus lowering the process cost from 1.76 $/L to 1.31 $/L (Kang et al., 2019). The energy obtained from burning the remaining lignin with other solid waste can meet the energy demand, which could reduce the overall production cost.

The recyclability and reusability properties of DES add an advantage to this green solvent at the industrial level. The cost can compensate for the recovery and production of the pretreated waste liquids (Chen et al., 2021a, 2021b). Since the building and disintegration of hydrogen bond linkage between the HBA and HBD occur during DES recovery and they are more easily recycled than ILs (Satlewal et al., 2018). Furthermore, developing economical and environmentally friendly DES pretreatment in the existing biorefinery depends critically on the cyclic usage of DESs. Modification of chemical composition and efficiency of enzymatic saccharification were used to assess the recycling capacity of the DES pretreatment (ChCl: Gly) combined with $FeCl_3$ at the optimum condition (120 °C; 6 h; 10 wt% biomass loading) on hybrid *Pennisetum* (Huang et al., 2020a, 2020b). The high discharge of lignin (78.88 wt%) and hemicelluloses (93.63 wt%) under the synergistic impact of Lewis acid and appropriate hydrogen bond of DES with $FeCl_3$ were primarily responsible for the good performance of pretreatment. Besides, even after five recycling steps, practically all cellulose can still be effectively converted into glucan. Therefore, DES is a priceless, recyclable pretreatment solvent that may support large-scale industrialization of biorefinery and make it easier to use biomass for the production of value-added products. Still, the studies on the recycling of DES were mostly done for five cycles. More than that, the formation of impurities limits the performance of DES pretreatment. Hence, further studies are needed for the improvement of the DES recycling process.

The high viscosity of DES leads to the absorption of water from the atmosphere or the biomass during pretreatment, altering the DES characteristics (viscosity and polarity) that affect the efficiency of the process. Therefore, an appropriate volume of water is added to inhibit the alteration of the DES performances. This may cause merits (increased viscosity, efficiency and process feasibility) and demerits (decreased delignification and collision frequency with biomass), which add up to the main challenges to the pretreatment. Therefore, optimization of water addition is a crucial factor. Another novel strategy to mitigate the energy and usage of water is the one-pot process. The chemical residues on the surface of the biomass must be removed using a significant volume of ethanol or water in standard solid-liquid separation (SLS) processing. These biomass washings use a significant amount of energy and produce a lot of wastewater. The pretreatment and saccharification in a one-pot process (PSOP) approach was used to overcome these issues. Consequently, this strategy reduces water usage, cost-effectiveness, prevents carbohydrate loss, and overall energy savings (13–15 folds) (Huang et al., 2020a, 2020b; Xu et al., 2016a, 2016b).

6. Conclusion

DES is considered a green solvent due to its advantages over other conventional methods, especially due to its low cost. Different types of DESs showed significant results in removing lignin and recovering glucose based on various optimum conditions. Still, more research is required to combine DES and other methods are necessary to identify the optimal process for the complete fractionation of the biomass and production of bioproducts. Moreover, it is critical to conduct more studies to understand the mechanism of pretreatment to maximize process efficiency. Furthermore, the techno-economic analysis is necessary to evaluate the feasibility of the process before the process is transferred to industrial-scale production. This review may assist the researchers in developing novel combinations of DES and improving the properties of the present available DESs by altering the operation condition for various types of biomass as a feedstock for the biorefining process.

CRediT authorship contribution statement

Jose D: Conceptualization, Investigation, Writing - Original draft, **Tawai A:** Data curation, Reviewing and Editing, **Divakaran D:** Reviewing and Editing, **Bhattacharyya D:** Reviewing and Editing, **Venkatachalam P:** Reviewing and Editing, **Tantayotai P:** Reviewing and Editing, **Sriariyanun M:** Conceptualization, Data curation, Reviewing, Editing, and Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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