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Review

Deep Eutectic Solvent Pretreatment and Green Separation of Lignocellulose

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Abstract: Plant-based waste biomass with lignocellulose as an important component is produced in large quantities worldwide every year. The components of lignocellulose that typically exhibit high utilization value include cellulose and hemicellulose, as well as pentoses and hexoses derived from their hydrolysis. As a pretreatment for the hydrolysis process, delignification is a pivotal step to enhance cellulose/hemicellulose accessibility and achieve high yields of fermentable sugars. Additionally, deep eutectic solvents (DESs) are the most widely used solvents for delignification during biomass fractionation due to their clean and environmentally friendly attributes. DESs dissolve lignin by inducing a large amount of β-O-4 bond cleavage and partial carbon–carbon bond cleavage, retaining cellulose in the solid residue, while most of the hemicellulose is hydrolyzed in DES pretreatment. This article provides a comprehensive review of the influence of DESs in the lignocellulose separation process. Key factors such as lignin removal rate, sugar conversion rate, and product chemical structure are critically reviewed to assess the feasibility of employing DESs for lignocellulose separation.

Keywords: lignocellulose; deep eutectic solvents; lignin separation; sugar conversion rate; chemical structure

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1. Introduction

Lignocellulosic biomass stands as a plentiful and renewable resource, poised to play a pivotal role in facilitating the sustainable production of fuels and chemicals in the foreseeable future [1]. According to 2022 statistics, the global annual production of lignocellulosic biomass is about 181.5 billion tons, of which only 8.2 billion tons of lignocellulosic biomass are utilized in productive applications rather than being treated as waste [2]. In 2024, the global lignocellulosic biomass market size is estimated at $4.3 billion and is expected to reach $9.1 billion by 2034. As one of the lignocellulosic components, the market for lignin is expected to grow at a compound annual growth rate (CAGR) of 4.5 from 2024 to 2030. [3]. Lignocellulosic biomass comprises cellulose, hemicellulose, and lignin, with the latter exhibiting a notably more intricate structure compared to cellulose and hemicellulose [4,5]. The typical structure of lignocellulose in plant-based biomass is a shell of cellulose and hemicellulose surrounded by interconnected lignin molecules [6]. The proportion of cellulose, hemicellulose, and lignin is slightly different in different parts of plants due to functional differentiation [7]. For example, hardwood biomass typically possesses a cellulose content ranging from 43% to 47%, hemicellulose content between 25% and 35%, and lignin content spanning from 16% to 24% [8]. Conversely, herbaceous biomass exhibits a composition characterized by cellulose levels of 33% to 38%, hemicellulose content ranging from 26% to 32%, and lignin content comprising 17% to 19% of its composition [9]. Agricultural and vegetable wastes such as fruit shells and pits often contain high amounts of lignocellulose. For example, the composition of cellulose, hemicellulose, and lignin of durian shell were 25.7 ± 1.9% (*w*/*w*), 18.5 ± 1.04% (*w*/*w*), and 15.9 ± 0.19% (*w*/*w*), respectively [10].

The separation and purification of lignocellulose components provide a possibility for efficient utilization and valorization of plant-based biomass waste [11]. A range of chemical treatments has been suggested for the separation of lignin components during biomass fractionation, including methods employing organic solvents [12] and ionic liquids [13,14]. Ionic liquids [13] are generally defined as compounds consisting entirely of ions with a melting point below 100 °C. They are preferred over conventional volatile solvents and catalysts from both "green" and "design" perspectives [15]). While ILs have demonstrated high separation rates for lignocellulose, their high cost and environmental unfriendliness preclude their widespread adoption as solvents for large-scale green production processes [16,17]. Recently, deep eutectic solvents (DESs) have emerged as viable alternatives, demonstrating their efficacy as environmentally friendly and sustainable biomass solvents [18,19]. The interaction between DESs and biomass can be understood as an acid–base catalytic mechanism [20]. The unstable ether–alkyl bonds between the phenylpropane units of lignin, as well as the hydrogen bonds and covalent bonds between lignin and hemicellulose are cleaved under the catalysis of hydrogen protons [21,22]. DESs typically consist of transparent fluids composed of at least two components, including one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) [23,24]. DES comprises large and asymmetric ions, and the reduction in lattice energy due to hydrogen bonds and charge delocalization leads to a lower melting point of the DES mixture compared to its individual components [25,26]. The degree of decline in melting point can be quantified as the difference between the melting point of binary mixture of component A and component B and that of the theoretically ideal mixture, denoted as ΔT_f. As illustrated in Figure 1, ΔT_f is directly correlated with the strength of interaction between components A and B. Greater interaction results in a lower melting point of the mixture, leading to a larger ΔT_f. Mixtures at specific molar ratios will exhibit the lowest melting point, known as the eutectic point [27]. The low melting point and high fluidity of DESs, along with its capacity to induce numerous β-O-4 bond cleavages in lignin structure and partial carbon-carbon bond cleavages (such as β-β′, β-5′), render it an efficient solvent for delignification, which is important in lignocellulosic separation processes [28]. There have been more than 1000 studies on the application of DESs in lignocellulosic separation in the past decade and it has received increasing attention from researchers since 2018. The cellulose separated and purified from lignocellulose is depolymerized into glucose and further converted into bio-based chemicals such as ethanol, furan dicarboxylic acid, caprolactam, sorbitol, levulinic acid, γ-valerolactone [29–32], 5-hydroxymethylfurfural (5-HMF) [33,34], 2-furfural (2-F) [33], and 2,5-Bishydroxymethylfuran (BHMF) [35], which become an important direction of value-added conversion of waste biomass. DES has been widely discussed and studied in recent years and has been applied in many practical applications as a new solvent. For example, Lee et al. investigated the ability of hydrophobic DES to extract non-polar compounds [36]. Vasil et al. investigated the superiority of DES as an early sample preparation step for atomic absorption spectrometry [37].

This paper provides a comprehensive review of the research and application of deep eutectic solvent (DES) in lignocellulose separation over the past decade (2014–2024). The review focuses on assessing the impact of DES on delignification efficiency and subsequent sugar conversion. Investigations delve into understanding the effects of DES composition, treatment conditions, and pretreatment measures on lignocellulose separation. Furthermore, the recycling capabilities and environmental sustainability of various DES formulations are evaluated.

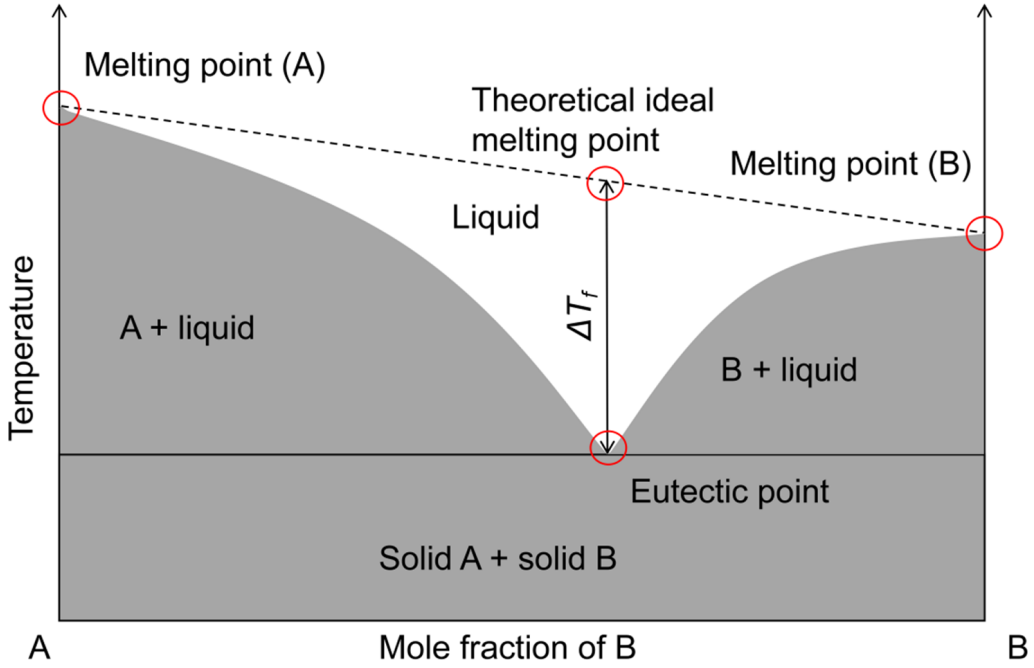

Figure 1. Schematic representation of a eutectic point on a two-components phase diagram.

2. Deep Eutectic Solvent in Separation of Lignocellulose

Various types of deep eutectic solvents (DESs) have proven effective in facilitating the separation of lignocellulosic materials [38]. Nonetheless, mechanical and chemical pretreatments have been employed in conjunction to enhance the separation efficiency and refine the process conditions, including the duration and temperature of the separation [39]. Table 1 provides an overview of the typical DES-based lignocellulosic separation systems that have been utilized in recent years, highlighting their key features and applications. It is noteworthy that type II DES (ChCl:$AlCl_3 \cdot 6H_2O$/$FeCl_3 \cdot 6H_2O$) and type III DES (ChCl:lactic acid/p-TsOH) are commonly employed in the lignin removal process. This is due to the limited low-melting-point range of non-hydrated metal halides forming type I DES, which results in higher costs compared to metal salts meeting the requirements of type II DES. The preparation of type III DES is simple, relatively unreactive with water, and cost effective. Additionally, many are biodegradable in line with Green Chem principles. The discovery of type IV DES has demonstrated that transition metal halides can also form eutectic crystals. However, their high melting point makes them challenging for use in lignocellulose separation [40,41]. Among these, type III DES has shown outstanding in effectively removing lignin [42].

By exploring the separation of lignocellulose with different DESs, researchers have observed that various classes and ratios of DES can effectively separate lignocellulose from different plant biomass. The specific separation effect is influenced by both the raw materials and types of DES used. Increasing the separation temperature and extending the separation time can improve the removal rate of lignin. Different chemical and mechanical pretreatments assist in enhancing the efficiency of lignocellulose separation.

Table 1. Delignification rate of different DESs for biomass and component ratio of solid residue.

Substrate	Solvent (mol)	Assisted Treatment	Condition	Delignification Rate (%)	Lignin in Solid Residue (%)	Cellulose in Solid Residue (%)	Hemicellulose in Solid Residue (%)	Cellulose Preservation (%)	Ref.
Alkaline DESs									
Industrial xylose residue	ChCl: MEA (1:6)	Microwave-assisted	80 °C, 10 min	91.95	3.59	95.60	0.42	98.73	[23]
Wheat straw	LA: Pyrazole (1:1)	-	145 °C, 9 h	93.70	2.15	-	-	51.17	[43]
Populus	ChCl: Imidazole (3:7)	-	150 °C, 0.67 h	75.50	6.50	29.90	2.90	69.25	[44]
Rice straw	ChCl: Urea (1:2)	-	130 °C, 6 h	43.19	8.43	25.06	11.55	70.61	[45]
Wheat straw	GL: Urea (1:2)	Hydrothermal pretreatment	90 °C, 3 h	75.60	19.80	76.13	nd	99.20	[46]
Neutral DESs									
Garlic skin	ChCl: GL: $AlCl_3 \cdot 6H_2O$ (1:2:0.2)	Ultrasound + microwave assisted	Room temperature, 30 min; 80 °C, 20 min	90.14	5.15	48.52	29.44	79.75	[47]
Sugarcane bagasse	ChCl: GL: $FeCl_3 \cdot 6H_2O$ (1:1:0.3)	Ultrasound ethanol pretreatment	240 W, 1 h; DES: 120 °C, 3 h	86.39	9.04	66.17	-	-	[48]
Bamboo	ChCl: Xylitol (1:2)	1 wt% H_2SO_4	120 °C, 4 h	84.91	10.72	73.30	1.82	72.68	[49]
Sugarcane bagasse	ChCl: PEG 600 (1:4)	1 wt% HES	170 °C, 2 h	83.23	11.41	75.66	nd	73.63	[50]
Corn straw	ChCl: 1,4-butanediol (1:2)	NaOH assisted	100 °C, 3 h	81.30	-	-	-	71.50	[51]
Industrial xylose residue	ChCl: IPA (1:6)	Hydrogen peroxide assisted	60 °C, 2 h	97.11	1.31	91.88	2.52	-	[16]
Acid DESs									
Poplar sawdust	ChCl: p-TsOH (1:2)	NaOH treatment	100 °C, 40 min	92.20	4.69	87.50	1.61	92.98	[52]
Poplar residues	ChCl: p-TsOH (1:2)	Ethanol	90 °C, 1 h	90.99	-	-	-	90.47	[53]
Poplar wood chips	ChCl: p-TsOH (1:2)	Ball milling	Room temperature, 3 h	99.78	-	-	-	82.19	[54]
Sorghum straw	ChCl: LA (1:1)	NaOH 0.75 wt% pretreatment	NaOH:121 °C, 1 h DES:140 °C, 0.67 h	79.30	11.20	53.40	29.30	79.67	[55]

Table 1. *Cont.*

Substrate	Solvent (mol)	Assisted Treatment	Condition	Delignification Rate (%)	Lignin in Solid Residue (%)	Cellulose in Solid Residue (%)	Hemicellulose in Solid Residue (%)	Cellulose Preservation (%)	Ref.
Corn stover	ChCl: LA (1:2)	Microwave-assisted	800 W, 45 s	79.60	9.22	65.78	5.03	75.11	[56]
Sugarcane bagasse	ChCl: LA (1:2)	Hydrothermal pretreatment	130 °C, 1.5 h	84.30	3.50	78.50	10.60	56.76	[57]
Corncob	ChCl: LA (1:2)	-	110 °C, 24 h	95.50	-	77.80	-	-	[58]
Eucalyptus grandis	ChCl: LA (1:2)	-	150 °C, 1.5 h	93.00	8.90	78.4	nd	49.47	[59]
Oil palm empty fruit bunch	ChCl: LA (1:5)	-	120 °C, 8 h	88.00	4.70	71.40	nd	-	[60]
Sugarcane bagasse	ChCl: LA (1:10)	Ultrasound	40 kHz, 1.5 h DES:120 °C, 3 h	86.82	6.89	65.62	4.47	67.57	[61]
Corncob	ChCl: LA (1:10)	-	130 °C, 4 h	95.90	1.5 0	74.90	7.00	89.03	[62]
Poplar	ChCl: LA (1:10)	PTA	120 °C, 4 h	82.20	-	-	-	-	[63]
Poplar sawdust	ChCl: LA (1:10)	Hydrothermal pretreatment	130 °C, 1.5 h	84.40	7.80	79.20	10.20	86.10	[64]
Poplar	ChCl: acetic acid (AA) (1:2)	-	130 °C, 3 h	76.50	9.50	85.40	6.90	99.00	[65]
Bamboo	ChCl: acetic acid (1:2)	-	140 °C, 6 h	80.10	7.30	-	-	92.70	[66]
Reed straw	BTEAC: FA (1:6)	1,4-dioxane/water (96:4 *v*/*v*)	130 °C, 3 h	94.10	9.00	89.32	1.68	88.57	[67]
Radiata pine	BTEAC: FA (1:2)	-	150 °C, 2 h	87.00	7.41	82.69	6.02	88.23	[68]
Corn stover	BTEAC: LA (1:7)	-	140 °C, 1.5 h	83.51	9.47	67.07	4.66	87.71	[69]
Pine wood powder	ChCl:LA: FA (1:1:1)	-	130 °C, 6 h	72.00	15.20	63.40	10.30	83.84	[70]
R. glutinis	ChCl: GL: Acetic acid (1:2:1.5)	-	140 °C, 4 h	63.76	7.29	55.6	23.91	78.00	[71]
Bamboo	GL: GndHCl: $FeCl_3 \cdot 6H_2O$ (2:1:0.2,)	Microwave-assisted	120 °C, 10 min	81.17	11.13	74.37	6.03	90.96	[72]
Poplar	ChCl: EG: 4-CSA (1:2:0.7)	KOH pretreatment	90 °C, 0.5 h	97.01	1.05	93.33	4.38	95.02	[6]
Pine needles	LA: Oxalic acid: ChCl (4:1:1)	Toluene-ethanol pretreatment	120 °C, 3 h	95.80	-	-	-	-	[73]

Table 1. *Cont.*

Substrate	Solvent (mol)	Assisted Treatment	Condition	Delignification Rate (%)	Lignin in Solid Residue (%)	Cellulose in Solid Residue (%)	Hemicellulose in Solid Residue (%)	Cellulose Preservation (%)	Ref.
Corn stover	ChCl: Oxalic acid: EG (1:0.2:2)	Densification pretreatment	130 °C, 1 h	75.27	7.85	59.43	11.09	88.75	[74]
Wheat straw	ChCl: CA: EG (1:1:2, mol)	-	100 °C, 12 h	92.37	5.71	89.12	3.04	89.18	[75]
Paddy husks	EG: CA (1:2)	-	90 °C, 16 h	52.35	15.25	44.00	17.37	-	[13]
Poplar sawdust	$ZnCl_2$: LA (1:10)	-	140 °C, 3 h	97.50	2.20	92.50	2.70	93.84	[76]
Canola straw	CTAB: LA: $FeCl_3$ (1:4:0.012)	-	180 °C, 2 h	87.40	8.70	59.40	2.10	53.89	[77]

Choline chloride: ChCl; lactic acid: LA; citric acid: CA; ethylene glycol: EG; glycerol: GL; formic acid: FA; monoethanolamine: MEA; 4-chlorobenzene sulfonic acid: 4-CSA; Isopropanolamine: IPA; Guanidine hydrochloride: GndHCl; Hydroxyethyl sulfonic acid: HES; Phosphotungstic acid: PTA; benzyltriethylammonium chloride: BTEAC.

3. Definition of Deep Eutectic Solvent Effects

In the current research on lignocellulose separation by DES, it is widely recognized that DES acts by disrupting chemical bonds, hydrogen bonds, and covalent bonds within lignin in biomass materials as well as between lignin and hemicellulose, thereby facilitating the separation of lignocellulose components. By comparing the lignin removal efficiency of different DES, it is evident that the binary systems of ChCl (choline chloride) + Alcoholamine/benzene sulfonic acid and some quaternary ammonium salt + Brønsted acid/Lewis acid have higher lignin removal capabilities [21,78]. The principle can be attributed to several factors: alkaline and acidic DES have excellent lignin solubility, and alkaline DES has the additional benefit of protecting polysaccharides in the material [23,79]. Benzene sulfonic acid demonstrates a significant lignin removal rate at relatively low temperatures due to its strong proton-supplying capacity, which increases its ability to solubilize lignin [6,80]. Furthermore, ternary DES is often used to increase lignin and hemicellulose removal rates [81], and when Brønsted and Lewis acids coexist in DESs, these two different acids can work synergically to destroy the lignocellulose structure and catalyze the cleavage of hemicellulose β-1, 4-glucoside bonds [77]. This combination of properties and synergistic effects makes these DES formulations particularly effective for lignocellulosic separations.

Due to the easy degradation of hemicellulose into toxic compounds in a strong acidic environment, such as furfural or acetic acid, and the low yield of aromatic monomers caused by lignin recondensation [82], recent research has focused on reducing the intensity of component degradation and condensation while maintaining a high degree of lignocellulose separation [83]. This approach aims to enhance lignocellulose reuse and the downstream conversion of compounds in crop residues. One promising strategy is to introduce polyols into acidic DES to form a mixed-solvent system that preserves the chemical structure of the isolated components. For instance, Ji et al. developed a polyol-based DES composed of ChCl, glycerol, and $AlCl_3 \cdot 6H_2O$, which successfully removed over 90% of lignin from garlic skin [48]. Shen et al. utilized a DES composed of ChCl, oxalic acid, and ethylene glycol to remove lignin from corn stover, which obtained better cellulose preservation and shortened the reaction time [74]. Similarly, Wang et al. used the neutral DES of ChCl/Xylitol and moso bamboo to obtain a lignin removal rate of about 85% [49]. The enhanced performance of these DES systems can be attributed to the presence of hydroxyl groups in the structure of polyols, which significantly boost the hydrogen bond supply capacity of the DES. This increased capacity for hydrogen bonding facilitates higher lignin removal rates [84]. As a binary neutral DES composed of HBD, polyols exhibit high cellulose preservation and monosaccharide conversion due to their mild chemical properties [85]. However, to overcome the limitation on lignin removal, dilute acids are usually used to pretreat raw materials [86]. On the other hand, polyols can be combined with quaternary ammonium salts and Brønsted/Lewis acids to form ternary acid DES. In these systems, polyols can be used as pH regulators to balance the lignin removal ability and component structure protection ability. Furthermore, DESs typically exhibit high viscosity, especially at close to room temperature, which can hinder mass transfer and prolong lignin removal times. The addition of polyols effectively reduce the viscosity of most DESs to improve its mass transfer efficiency and shorten the lignin removal time [87].

Many kinds of assisted treatments are used in lignocellulosic separation processes [88]. Different treatments often have varied effects on the separation process and the material [89,90]. For example, microwave and ultrasonic treatments provide distinct advantages over conventional conduction and convective heating methods [91,92]. Microwave radiation can transfer heat more quickly and evenly through dipole rotation and ion conduction with lower energy loss, which greatly reduces the reaction/extraction time without compromising the ease of control [93]. In addition to directly interacting with polar molecules in DES, microwave energy can selectively heat polar portions of biomass. At the same time, it improves the interaction between DES and lignin, and microwave-induced molecular scale stirring and mixing increases the mass transfer rate, making lignin easier to extract and dissolve [94]. The special cavitation effect of ultrasound can change the structure and

properties of biomass during treatment [95]. For lignocellulose, ultrasound treatment can destroy the outer structure of the lignin, separate out the hemicellulose and increase the accessibility of cellulose molecules [96]. Some studies have found that the yield of reducing sugar from biomass is increased by enzymatic hydrolysis or acid hydrolysis after ultrasonic pretreatment [97].

Pretreatment or assisted separation of lignocellulosic raw materials using chemical agents such as acids, bases, or alcohols has been shown to be an effective way to improve the separation efficiency. Huang et al. [50] added 1 wt% hydroxyethyl sulfonic acid to DES of ChCl/PEG 600 to construct an acid lignocellulosic separation system and isolated more than 83% lignin and almost all hemicellulose from sugarcane bagasse. This proved that acidic environment can significantly improve the separation effect of lignocellulose [98]. Zhou et al. [6] achieved more than 97% and 87% removal rates of lignin and hemicellulose from poplar by KOH pretreatment. It was found that the BET (Brunauer–Emmett-Teller) surface area of the pretreated material increased and the contact angle between poplar and DES decreased, which increased the subsequent lignin removal rate [6].

Alkaline hydrogen peroxide pretreatment (AHP) has good performance in biomass deconstruction. It is beneficial to moderate the processing conditions of DES. The main mechanism of action is the dissociation of H_2O_2 under alkaline conditions to produce highly reactive oxygen species (ROS), such as hyperhydroxylated anions (HOO-) and free radicals (HO·). ROS depolymerizes lignin by attacking the lignin side chain and reacts with the enone chromophore (such as the quinone structure) in lignin to increase the dissolution of lignin and reduce the polymerization of lignin [99]. Ma et al. [16] used hydrogen peroxide to pretreat industrial xylose residue at 60 °C, removing more than 97% of lignin. This has greatly reduced the energy consumption in the separation process compared to similar raw materials without pretreatment.

Mechanochemical pretreatment processes have been increasingly recognized as green methods for deconstructing lignocellulose through mechanical forces such as shock, compression, shear, and friction [100]. Ball milling has been widely used in research and industry as a mechanical treatment to break and reduce sample particle size. In biomass pretreatment, ball milling can effectively deconstruct materials and increase the contact area between lignocellulosic components and DES, thus accelerating the separation rate [101]. This characteristic makes ball milling a method to simplify the separation conditions of lignocellulose [102]. Impressively, Sun et al. used DES to remove lignin from poplar wood during ball milling, achieving a removal rate of over 99% at room temperature [54].

Hydrothermal pretreatment is a straightforward and effective method that relies solely on the addition of water, making it widely used in the processing of lignocellulosic biomass [103]. Its simplicity offers an opportunity to reduce production costs [104]. Hydrothermal pretreatment is a chemical-free, economical and environmentally friendly process with little effect on the structure of lignin and cellulose. In addition, hydrothermal pretreatment uses water at high temperatures and pressures to hydrolyze the lignocellulosic structure, especially hemicellulose, which is more easily hydrolyzed due to its highly amorphous structural properties [105]. Compared to biomass material, the pretreatment significantly shortened the treatment time while maintaining the same lignin removal rate [57,64].

Overall, different types of DESs have varied separation effects on biomass due to their specific compositions and ability to disrupt and catalyze the breakdown of lignocellulosic structures. By modifying the components of DESs and introducing assisted solvent, the lignin solubility of DES can be adjusted, thereby protecting the structure and function of raw materials after separation [106]. Numerous of assisted treatment methods have been applied to lignocellulosic separation process [107]. The assisted treatment can improve the separation capacity of DES or simplify the separation conditions through chemical or physical means [108]. By comparing the different kinds of auxiliary treatment on the separation effect of lignocellulose, it can be found that microwave-assisted pretreatment and

ball-milling pretreatment often have a higher lignin removal rate and cellulose retention rate. This is due to the potential of these two methods to be applied in industry.

Figure 2 provides a comprehensive and intuitive overview of the steps involved in the separation of lignocellulosic biomaterials using DES. This includes the composition and type of DES, pretreatment of biomass, separation of lignocellulose by DES, and the resulting cellulose-enriched residue and lignin-enriched filtrate obtained through filtration. Due to the high viscosity of DES, an organic solvent-assisted filtration process is necessary to effectively separate the cellulose-enriched component from the DES + lignin/hemicellulose component. Commonly used organic solvents in such studies include aqueous solutions of ethanol or acetone [49,51], which serve to reduce the viscosity of the filtrate without causing dissolution of solid cellulose residues. The changes in biomass microstructure during DES treatment were analyzed by SEM after drying the solid residue. At present, DES is widely used as a catalyst, co-solvent, and extraction solvent for various conversion and downstream processes [109].

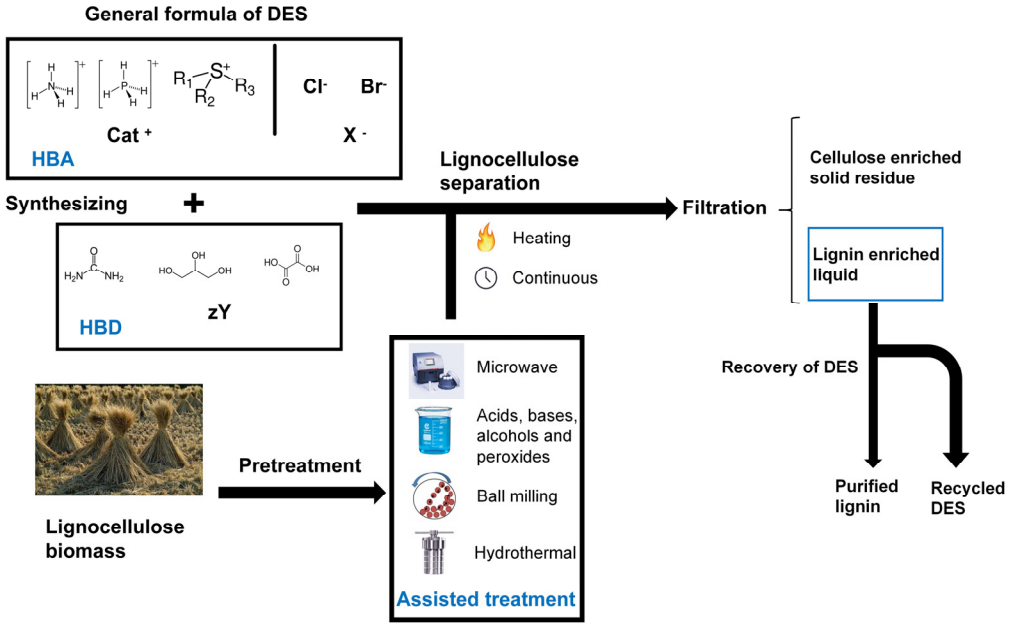

Figure 2. DES separation process of lignocellulose. Cat^+ for ammonium and other cation, X^- for Lewis base, generally a halide anion, Y stands for Lewis or Brønsted acid (z refers to the number of Y molecules that interact with the anion).

The recycling of DES is one of the major challenges in achieving cost-effective industrial applications [110,111]. The relatively low solvent consumption and recyclability of DES make it an important green solvent in the field of green separation of lignocellulose [112]. There are many methods to recover and purify DES, including the addition of anti-solvent, crystallization, membrane filtration, solid–liquid extraction, liquid–liquid extraction, short path distillation, supercritical fluid extraction, and density differences-based separation [24,113–117]. Specific recovery methods can be selected based on the types and characteristics of DES, the properties of target compounds, energy consumption, and equipment costs [118–122]. Although DES is widely known as a green solvent, it does not remain environmentally friendly under all conditions due to decomposition and volatilization. Therefore, many strategies have been studied and applied to improve the greenness of DES as potential solutions to achieve Green Chem [123]. For example, strategies include choosing more natural ingredients [121,124], specific functionalization [125], increasing molecular weight and surface area by polymerization for separation, sensing and catalysis [126], tuning types of intermolecular interaction and component numbers [127], constructing a switchable system for efficient separation [128], avoiding air, water, high

temperature, reduced pressure, strong oxidizers/deoxidizers, long-term exposure, and organic solvents [129].

4. Effect of DES on Sugar Conversion of Substrate

It is found that the reducing sugar yields from the pretreated cellulose-enriched solid residue differ from those of the untreated biomass [130]. Untreated biomass contains both cellulose and hemicellulose. However, after pretreatment with DES, the biomass generally no longer contains hemicellulose. Figure 3 completely shows the enzymatic hydrolysis process of lignocellulose isolated after DES pretreatment to produce glucose. It is worth noting that DES treatment removes lignin and hemicellulose in biomass, which significantly improves the enzymatic hydrolysis rate of cellulose enriched residue after treatment.

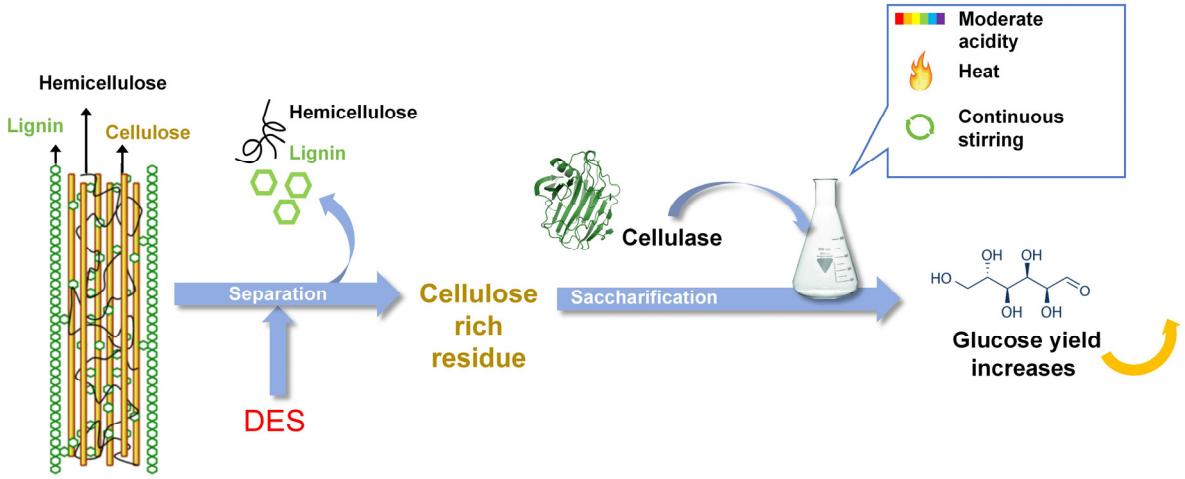

Figure 3. Schematic diagram of enzymatic hydrolysis of cellulose enrichment residue after DES pretreatment.

Table 2 shows the changes in enzymolysis glucose yield of lignocellulosic biomass substrates before and after pretreatment with different types of DES. It is evident that each DES pretreatment significantly improves the substrate enzymatic hydrolysis efficiency between (174–883)% with different types of cellulase [16,23,56,131–134]. It is worth noting that adding appropriate metal chloride salts or benzene sulfonic acid to DES as an auxiliary solvent can further significantly improve the glucose yield compared to conventional binary DES. Wu et al. added 1.6 wt% p-TsOH to soybean straw as pretreatment in BTEAC/glycerol system, which increased the yield of substrate glucose hydrolysis from 9.17% to 90.18% [131]. These findings are interpreted as the disruption of the complex structure of biomass, degradation of hemicellulose, and removal of lignin after pretreatment with DES. This pretreatment strategy resulted in the destruction of the hemicellulose–cellulose binding protein matrix, exposing more enzyme attack sites, and improving the accessibility of substrate enzymes [72,133].

Table 2. Effects of pretreatment of lignocellulosic biomass with DES pretreatment system on reducing glucose yield.

Substrate	DES	Condition	Untreated Glucose Yield (%)	DES-Treated Glucose Yield (%)	Increase Rate (100×%)	Ref.
Switchgrass	ChCl: lactic acid 1:2	Solid loading 1.5 wt%, 20 mg protein/g solid, CTec2:HTec2 = 1:9 (vol%)	13.61	75.0	4.51	[56]
Industrial xylose residue	ChCl: monoethanolamine 1:6	Solid loading, 5 wt%, 10 FPU/g CTec2	15.97	90.12	4.64	[23]

Table 2. *Cont.*

Substrate	DES	Condition	Untreated Glucose Yield (%)	DES-Treated Glucose Yield (%)	Increase Rate (100×%)	Ref.
Industrial xylose residue	ChCl: monoethanolamine 1:6	10 FPU/g CTec2	34.95	95.89	1.74	[16]
Sugarcane	ChCl: lactic acid 1:2	Solid loading, 10 wt%, 15 mg protein/g solid, cellulase enzymes NS22257	19.74	93.99	3.76	[132]
Corn stover	$FeCl_3$/ChCl: *N*-(2-hydroxyethyl) Ethylenediamine 1:4	Solid loading, 5 wt%, 30 FPU/g CTec2	16.54	98.6	4.96	[134]
Soybean straw	p-TsOH/BTEAC: glycerol 1:12	Solid loading, 5 wt%, 10 FPU/g, CTec2	9.17	90.18	8.83	[131]
Eucalyptus wood chips	$AlCl_3$/Betaine: lactic acid 1:2	30 FPU/g, CTec2	13.20	96.00	6.27	[133]

5. Effect of DES Treatment on the Chemical Structure of Lignocellulosic Separation Products

FT-IR spectroscopy can be used to study the effect of DES pretreatment on the internal chemical structure of lignocellulose by comparing the characteristic absorption peaks of chemical bonds such as CH, C-C, and CO [135]. This technique allows for the identification and quantification of functional groups present in the lignocellulosic material, providing insights into the chemical changes induced by the pretreatment process [63]. Xie et al. [136] pretreated Moso bamboo with ChCl/zinc acetate DES under microwave-assisted conditions and performed FT-IR characterization of the samples before and after treatment. The FT-IR results showed changes in lignocellulosic characteristic peaks associated with OH, CH, CO, and CO bond stretching. After DES pretreatment, the characteristic peak at 3331 cm^{-1} almost disappeared. This suggested that bands of intramolecular and intermolecular hydrogen bonds between 3500 and 3100 cm^{-1} were destroyed by DES. In addition, the absorbance of DES pretreated biomass decreased at 1734cm^{-1}. These peaks indicate removal of hemicellulose because they suggest stretching vibrations of acetyl groups in hemicellulose [137].

Li et al. [138] pretreated rape straw with ChCl/oxalate acid DES and performed FT-IR characterization of the samples before and after treatment. It was found that peaks near 3420 cm^{-1} were associated with tensile vibrations of OH in biomass lignin, and -CH_2 vibration was detected near 2930 cm^{-1}. The ester bond stretching vibration between hemicellulose and lignin was close to 1732 cm^{-1}. After pretreatment, the characteristic peaks at 3420 cm^{-1} and 2930 cm^{-1} were significantly reduced, indicating that the hydrogen bond within lignocellulose was broken. Additionally, the tensile vibration of aromatic ring-associated CO near 1625 cm^{-1} was significantly reduced, indicating the degradation of lignin in the raw material [139]. The peak near 1420 cm^{-1} was associated with the bending of -CH_2 in cellulose. Peaks near 1050 cm^{-1} corresponded to CO stretching in the hemicellulose–cellulose–lignin polymers. The peak near 896 cm^{-1} was associated with the β-glucoside bond. These FT-IR data indicated that DES pretreatment can effectively remove hemicellulose and lignin from biomass [140]. Table 3 clearly summarizes the chemical bond changes in the biomass after DES treatment of lignocellulose.

Table 3. The effect of DES pretreatment on the internal chemical structure of lignocellulose was studied by comparing the characteristic absorption peaks of chemical bonds with FT-IR spectroscopy.

Substrate	DES	Chemical Bonds	Absorption Peaks (cm^{-1})	Trend	Affected Component	Ref.
Moso bamboo	ChCl: zinc acetate = 1:6	OH/C-H	3331/2891	Almost disappeared	Hydrogen bonds	[136]
		C=O	1734	Decreased	Hemicellulose	
Rape straw	ChCl: oxalic acid = 3:1	CO	1625	Significantly reduced	Lignin	[138]
		CO stretching	1050	Reduced	Hemicellulose-cellulose-lignin polymers	
		CH or CH_2 bending	896	Reduced	β-glucoside bond	
Willow	ChCl: lactic acid = 1:10	CH bending vibration of aliphatic compounds	1373	Not present	Carbohydrates	[141]

DES pretreatment can significantly affect the types and contents of functional groups in lignocellulosic biomass, playing a crucial role in disrupting the interactions between lignocellulosic components and lignin structure [142]. The structural differences of regenerated lignin are usually analyzed by 2D-HSQC NMR [143]. In general, the major substructures of lignin include methoxy [120], aryl ether bonds (A, β-O-4), and β-β resinol (B). As Figure 4 shows, during the pretreatment process, the cleavage of β-O-4 linkage in lignin linkage significantly increased with the increase in pretreatment temperature. It was found that the β-O-4 bond disappeared above 110 °C, indicating that the depolymerization of lignin was achieved by destroying the β-O-4 substructure during DES pretreatment. This is also consistent with the results of acidic DES pretreatment and the breakdown of most lignocellulose. The lignin–carbohydrate complex (LCC) bond, as described above, shows different signals in the aromatic region corresponding to guaiacol (G) and syringyl (S) units, which are clearly visible. This phenomenon indicates the process of lignin polycondensation during pretreatment [144].

Morphological changes of lignocellulosic biomass during DES pretreatment can be analyzed by SEM. This technique provides detailed images of the surface structure and morphology of the biomass, allowing researchers to observe alterations at the microstructural level [145]. Moran-Aguilar et al. [146] pretreated sugarcane bagasse (SCB) with ChCl/carboxylic acid. The morphological changes of SCB surface after pretreatment were shown in Figure 5. Pictures of the natural samples showed smooth, complete, and ordered fiber surfaces (Figure 5a), while SEM analysis of the pretreated samples revealed structural differences, with rough and exposed structural morphology. Micrographs of ChCl/LA (lactic acid) showed smooth and consistent surfaces (Figure 5b), mainly indicating the presence of crystalline cellulose. The pretreated samples had higher crystallinity and more ordered cellulose structure than the natural samples [147]. In addition, images of ChCl/CA (citric acid) pretreated biomass indicated a planar porous structure and non-uniform surface formed by various fiber fragments (Figure 5c). Finally, images of the SCB pretreated with ChCl/AA (acetic acid) showed that the deformed structure had wide cracks and holes (Figure 5d). The loss of fibers and the increase in porous surfaces can be observed [146].

The effects of DES with different characteristics and the addition of auxiliary solvents on the morphology of biomass were also demonstrated by SEM analysis [148]. This technique showed that mild acidic DES pretreatment can improve cellulose reactivity by decomposing and swelling the cellulose, removing lignin and hemicellulose (mainly xylan), thereby better exposing the innermost cellulose component of the biomass and making it accessible to enzymes [149]. In contrast, alkaline DES can lead to expansion and partial dissolution of lignocellulosic materials. These DES systems typically effectively remove lignin while preserving the cellulose structure [150]. Shen et al. added $FeCl_3$ to Moso bamboo pretreated with ChCl/lactic acid DES. SEM illustrated varying degree of cracks and fragments on the surface of the fibers after pretreatment. $FeCl_3$-mediated pretreatment caused more

damage to cellulose, indicating that adding $FeCl_3$ can improve the intensity of biomass pretreatment [151]. Ma et al. added hydrogen peroxide to industrial xylose residue after ChCl/Isopropanolamine pretreatment. SEM images showed that as the hydrogen peroxide content increased, the pores in the pretreated substrate also increased. This indicated that hydrogen peroxide had destroyed the morphology of the residue while removing lignin, which helped improve the yield of fermentable glucose [16]. Grzegorz et al. explained the effect of microwave-assisted treatment on the microstructure of lignocellulose through SEM analysis. The results showed that microwave-treated biomass particles had larger porous structures on their surfaces, which exposed more cellulose structures. The pore structure and cellulose exposure contribute to the hydrolysis efficiency of cellulase [152]. Chemical treatment usually achieves the effect of separating components through targeted chemical bonding. However, ultrasonic and microwave treatments tend to destroy the biomass structure with physical impact. Both of them can increase the porosity of lignocellulose and improve the efficiency of enzymatic hydrolysis.

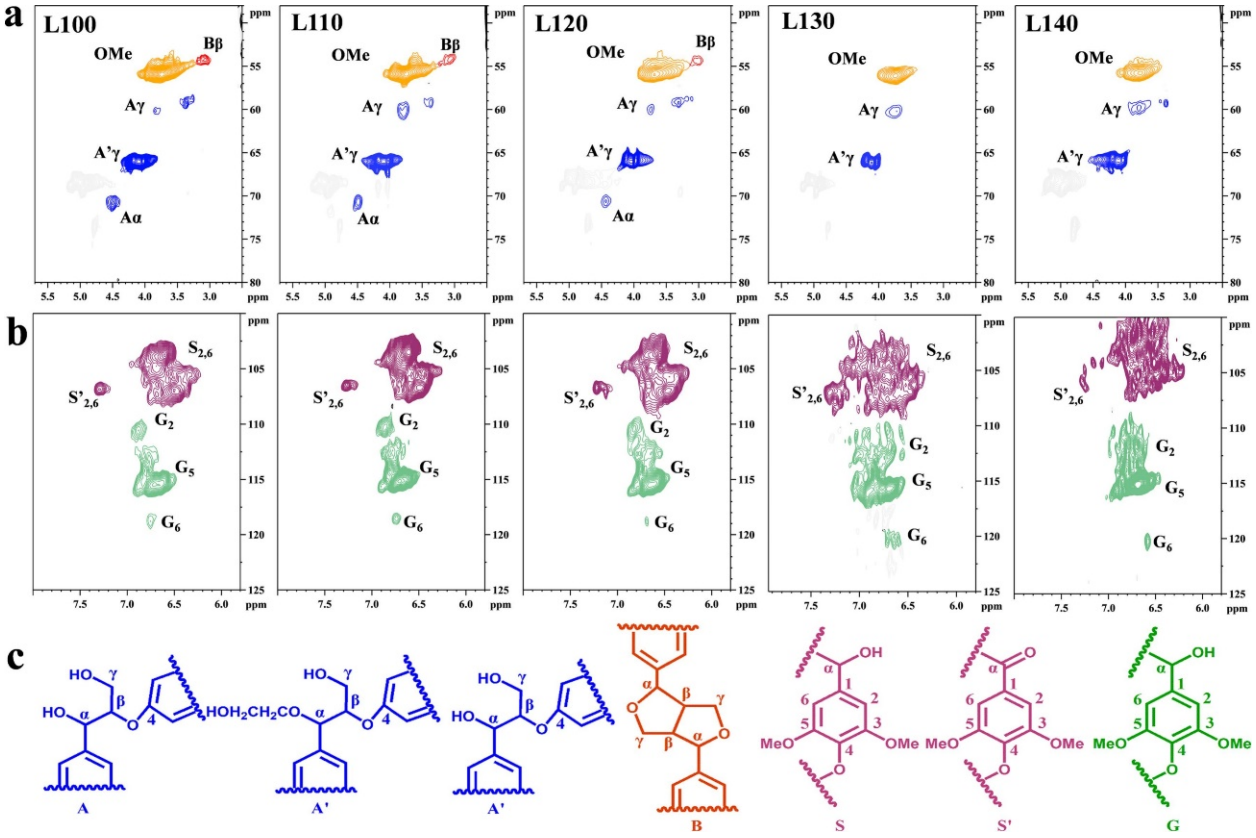

Figure 4. (**a**) Side-chain regions in 2D-HSQC spectra of the lignin, (**b**) aromatic regions in 2D-HSQC spectra of the lignin, (**c**) the identified main structures in the lignin (Reprinted/adapted with permission from Ref. [144]. 2023, Xuefeng Yao) [144].

Overall, FT-IR spectral analysis can be utilized to compare the presence or absence of characteristic peaks associated with specific functional groups before and after DES pretreatment. This alteration is employed to ascertain the chemical bonds that have been broken and new bonds that have been formed during the process. The side chain and aromatic regions of the 2D-HSQC spectra were analyzed. Trends in the increase and decrease in chemical bonds and units in polymers during DES treatment were determined by evaluating the sizes of the corresponding functional group graphs. SEM analysis can effectively demonstrate the effect of DES pretreatment on the morphology of lignocellulosic biomass. It can be observed that most DESs can cause the surface of the biomass to form porous and non-uniform structure by destroying the bonding bonds in the biomass.

Moreover, the addition of auxiliary solvents in the DES pretreatment process can also enhance the damage ability of the biomass surface, which can also be confirmed in the improvement effect of lignocellulose separation ability corresponding to this method in the previous section.

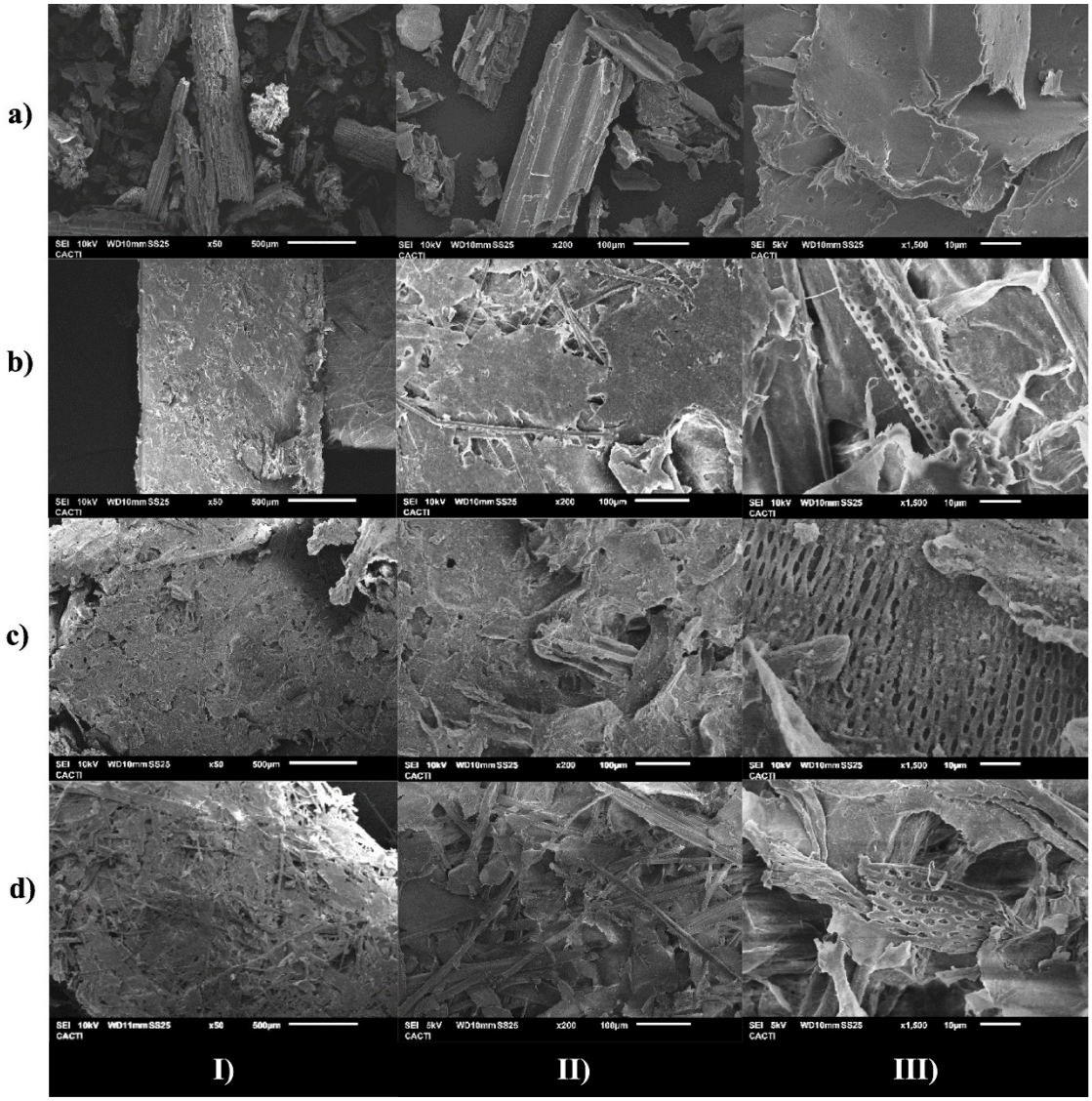

Figure 5. Images of (**a**) the native sugarcane bagasse (SCB) and SCB pretreated with different HBD of DES: (**b**) ChCl/lactic acid, (**c**) ChCl/citric acid and (**d**) ChCl/acetic acid. Micrographs were obtained with variable magnification: (I) ×50; (II) ×200; (III) ×1500 (Reprinted/adapted with permission from Ref. [146]. 2022, María Guadalupe Morán-Aguilar) [146].

6. Conclusions

Lignocellulose, which accounts for the majority of the waste biomass in crops and other plants, has become an important raw material for platform chemicals. To effectively use this waste biomass, it is necessary to separate lignocellulose into purified cellulose, hemicellulose, and lignin. In recent years, DES, as a green and easy-to-synthesize solvent, has received extensive attention from researchers. Different kinds of DESs have shown different lignin separation efficiencies due to their ability to supply proton and cleave hydrogen bonds and covalent bonds. Mechanical- or chemical-assisted treatments have been shown to optimize the separation conditions of lignocellulose, including reducing the reaction temperature and shortening the reaction time. The separation mechanism of

DES on lignocellulose can be better understood by analyzing the biomass before and after treatment through various characterization methods, paving the way for more effective and sustainable biomass conversion technologies. Although extensive research has been conducted on the separation and purification of lignocellulose from waste biomass and the reuse of products, there are still several challenges in optimizing the pre-/post-processing steps of separation from a green and economic perspective:

1. Prior to DES pretreatment, fat-soluble components in biomass can be eliminated through organic solvent or supercritical fluid extraction to enhance the efficiency of DES treatment.
2. Variations in the separation effect between different types of DESs and biomass have been observed, which are generally attributed to differences in their physical and chemical properties, including solvent polarity, proton-providing capacity, hydrogen bonding capacity, and electrical conductivity. The specific impacts of these properties require systematic exploration.
3. While the DES processing temperature has gradually decreased in previous studies, further investigation is needed to explore the potential for lower temperatures or even room temperature separation.
4. Attention should be given to assessing the impact of DES treatment on the chemical structure and crystallinity of lignin products as this influence can guide lignin towards meeting specific deep processing requirements.

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Abbreviations

DES	Deep eutectic solvent
CAGR	Compound annual growth rate
ILs	Ionic liquids
HBD	Hydrogen bond donor
HBA	Hydrogen bond acceptor
HMF	5-hydroxymethylfurfural
F	2-furfural
BHMF	2,5-Bishydroxymethylfuran
ChCl	Choline chloride
LA	Lactic acid
p-TsOH	p-Toluenesulfonic Acid
MEA	Monoethanolamine
GL	Glycerol
AA	Acetic acid
BTEAC	Benzyltriethylammonium chloride
FA	Formic acid
GndHCl	Guanidine hydrochloride
4-CSA	4-chlorobenzene sulfonic acid
OA	Oxalic acid
EG	Ethylene glycol
CA	Citric acid
HES	Hydroxyethyl sulfonic acid

IPA	Isopropanolamine
PTA	Phosphotungstic acid
CTAB	Cetyltrimethylammonium bromide
BET	Brunauer-Emmett-Teller
AHP	Alkaline hydrogen peroxide
ROS	Reactive oxygen species
FT-IR	Fourier Transform Infrared Spectroscopy
LCC	Lignin-carbohydrate complex
G unit	Guaiacol
S unit	Syringyl
2D-HSQC	2D-Heteronuclear Single Quantum Coherence
SCB	Sugarcane bagasse
SEM	Scanning electron microscope

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