Deep Eutectic-like Solvents: Promising Green Media for Biomass Treatment and Preparation of Nanomaterials

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Deep eutectic-like solvents (DESs) are recognized as environmentally benign media with highly tunable structures and properties. The usage of DES is promising in the field of biomass treatment and transformation, including pretreatment, selective dissolution, and separation of the main components. It serves as a green medium for modification of the biomass components, as well as preparation of biomass-derived nanomaterials. In this paper, the development on DES, including composition, properties, and characteristics was studied. The application of DES in biomass-derived nanomaterials is especially discussed. This review intends to provide references for adopting DES to improve biomass-based environmentally friendly nanomaterials.

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INTRODUCTION

With the development of society, the concept of eco-friendly industrial practices has become deeply rooted in people's hearts. In modern industrial society, the choices of green solvents are continually being explored. Supercritical fluids, ionic liquids, and so-called deep eutectic solvents have been shown to meet the environmentally benign requirement and with good practicability (Benvenutti *et al.* 2019; Choi and Verpoorte 2019; Clarke *et al.* 2018). Among them, deep eutectic-like solvent (DESs) have become the prominent choice, owing to the unique inherent characteristics, as tunable properties with different hydrogen bond donor and receptors, stable physicochemical properties, biocompatibility, recyclability, non-flammability, negligible vapor pressure, and the fact that they are easily manufactured, *etc.* (Zuo *et al.* 2019). The term "eutectic-like" is used in the present article due to the fact that most DESs reported in recent literature do not correspond to any minimum in temperature of melting. Rather, it has been discovered that certain blends having similar components to eutectic mixtures can have advantageous solubilization characteristics.

Recently, studies related to application prospects of DESs for biomass treatment and transformation are on an upsurge, especially with respect to isolation of the main components of biomass and obtaining nanomaterials (Sarmad *et al.* 2017; Galbe and Wallberg 2019; Wang *et al.* 2019; Hansen *et al.* 2020; Shishov *et al.* 2020; Musarurwa and Tavengwa 2021).

The concept, 'Deep Eutectic Solvent', was firstly put forward by Abbott and coworkers in 2003. They prepared a mixed solvent from choline chloride (ChCl) and urea having molar ratio of 1:2, which presented a melting point of 12 °C (Abbott *et al.* 2003). Since then, this kind of solvent has been utilized to achieve superior results as a class of green solvents. In 2014, Smith and coworkers categorized the DESs into four main types according to their compositions, as shown in Table. 1. Among them, the third type of DES has received the most attention, due to their biodegradable ingredients. Some of such DESs are even food grade. The food grade DESs are called Natural Deep Eutectic Solvents, which were named by Spronsen and coworkers in 2011 (Choi *et al.* 2011).

Table 1. The Four Categories of DES According to Smith *et al.* (2014)

Category	Constituent A	Constituent B
1	Imidazolium salt	Metal halides
2	ChCl	Hydrated metal halides
3	ChCl	Hydrogen bond donor
4	Metal halides	Hydrogen bond donor

It is obvious that a DES is usually formed by mixing a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in a certain molar ratio (Abbott *et al.* 2003; Benvenutti *et al.* 2019; Musarurwa and Tavengwa 2021). The regularly used species are summarized in Table 2. Under certain conditions, the whole solvent system forms a strong hydrogen bonded network, which lays the basis of the great properties. Furthermore, by selection of different HBDs and HBAs, by tuning mole ratios of the two main parts and introduction of cosolvent, *e.g.* deionized water, the physicochemical properties of the DES can be adjusted in most cases (Dai *et al.* 2015; Zhang *et al.* 2016; Elgharbawy *et al.* 2020). It follows that a DES system can be tailored according to various particular applications. With the joint efforts of numerous researchers, all kinds of DESs have been created up to the present. The constituents can be sugars, alcohols, amino acids, and carboxylic acid, *etc*. (Lu and Liu 2020; Tian *et al.* 2022).

Table 2. Summary of the Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA) Species in Various DESs

Hydrogen Bond Donor		Hydrogen Bond Acceptor	
Acids	Lactic acid Oxalic acid Citric acid Malic acid Malonic acid Levulinic acid P-toluenesulfonic acid Formic acid	**Alkaline**	ChCl Benzyltrimethylammonium chloride Benzyltriethylammonium chloride Dimethylethanaminium chloride Betaine
Alcohols	Glycerol Ethylene glycol Menthol Triethylene glycol	**Metal salts**	$ZnCl_2$, K_2CO_3
Others	Urea Imidazole Glucose		

The components of most DESs are environment-benign and have low toxicity. In particular, DESs with ChCl as HBA have received the most widespread attention due to their unique structure and naturally low toxicity, meaning that they have proved to be safe for foodstuffs and cosmetics (Lu and Liu 2020; Torregrosa-Crespo *et al.* 2020). ChCl-DESs are widely applied in biomass pretreatment, composition extraction, and separation, as well as other aspects. The DESs with the acids serving as HBD (acid-DESs) are an important part of the DESs system. In particular, the DESs with organic acids as HBD component, such as oxalic acid, and lactic acid, *etc.* (Ma *et al*. 2016; Shen *et al.* 2019; Tian *et al.* 2022) are usually used for the isolation of bioactive compounds from natural resources. At the same time, the hydrophilicity and hydrophobicity are important properties for DES. The hydrophilic DESs account for a large proportion of the recently reported applications, while the hydrophobic DESs were not reported until 2015 as water-immiscible extractants. According to Osch *et al.* (2015), hydrophobic DESs have been widely studied recently. They have been widely applied in extraction and chemical analysis, which are becoming an important direction (Xiong *et al*. 2019).

In this review, starting from the introduction of the characteristics and performances of DESs, the most potential and important applications of DESs as the green medium preparing in nano-biomass will be further described. The review will discuss how to make use of these properties of DESs with plant biomass, as well as the current situation and shortcomings. In addition, the practicability and possible mechanisms of DES implementation in scenarios will be discussed. Many efficient formulations and treatment methods will be summarized to lay a solid foundation for future studies of DESs in the field of biomass.

PREPARATION AND PROPERTIES OF DESs

Preparation of DESs

According to the requirement on properties, suitable methods can be selected. The key point for the preparation of DES is to form a stable hydrogen bond network, which then mainly affects the performance of the DES. The two most commonly-used preparation methods, as shown below, are rather convenient (Zdanowicz *et al.* 2018).

The first is conducted by simply heating and mixing the HBD and HBA thoroughly, with the formation of a transparent liquid. The other is the freeze-drying method (Gutierrez *et al.* 2009), in which, the two parts are dissolved in water respectively, then mixed to be frozen at low temperature, finally being dried into a clear and sticky mixture. For both of the methods, it usually is completely removed the moisture from the solution.

The two methods described above are suitable for most situations. Furthermore, there are other ways, such as evaporation heating method combined with grinding, or using an extrusion method (Dai *et al.* 2013; Crawford *et al.* 2016).

The Species of HBA and HBD

HBD/HBA species can be selected with different chemical structures, such as aromatic or aliphatic compounds, differences in chain length, different numbers of functional groups, *etc*. The molar ratio of the two parts is also an important factor affecting the properties of DESs (Zhang *et al.* 2016). According to Ma *et al.* (2016), during the treatment of corncob feedstock, with the different molar ratios of ChCl to different HBAs (oxalic acid, glycerol or ethylene glycol), the efficiency for lignin extraction could range from 59% to 98.5%. The polarity, hydrogen bonding, and acidity/alkaline properties of DES all affect the performances of components extraction (Hou *et al.* 2018; Kumar *et al.* 2018; Tan *et al.* 2019). The most commonly used DESs with choline as HBD always have high polarity (Elgharbawy *et al.* 2020). The usage of DES of high polarity is beneficial for biomass component extraction, enzymolysis, and saccharification (Zhang *et al.* 2016; Guo *et al.* 2018; Dugoni *et al.* 2020), which will be further discussed in the following part. At the same time, DESs are widely used in pretreatment of biomass raw materials. Guo *et al.* (2022) have compared the acidic-DESs consisting of formic acid/ChCl and lactic acid/ChCl with the alkaline-DESs that were made up of monoethanolamine/ChCl and glycerol/K_2CO_3. It was found that the delignification capacity with the acidic-DESs was much higher than the alkaline-DESs (more than 95%), and the alkaline-DESs could modify the lignin with introduction of amine groups in the process. For the most hydrophilic component of biomass—'hemicellulose', according to Yang *et al.* (2021), they prepared the DES with choline chloride and monoethanolamine. It was found to be an efficacious medium for deconstructing the recalcitrant structure of poplar under a mild condition. After that, they synthesized DESs from natural organic acids and common polyols (Yang *et al.* (2022), and these were adopted to deconstruct corncob successively for fractionation of hemicelluloses. This was shown to be an eco-friendly hemicellulose extraction process.

Viscosity

The viscosity of the solvent and medium affects the performance of DES considerably. Due to the continuous network of hydrogen bonding between the HBD and HBA constituents, DESs generally have high viscosity, which limits the mobility of the materials in DES media (Elgharbawy *et al.* 2020). Viscosity values of most current DESs are between 173 and 783 mPa·s at room temperature (Elgharbawy *et al.* 2020), and the viscosity index decreases with the rise of temperature. When the DES has high viscosity, that condition will seriously affect the interaction with biomass. To overcome the problem, water can be a useful candidate to be introduced in to decrease the viscosity (Dai *et al.* 2015; Kumar *et al.* 2016; Yiin *et al.* 2016; Florindo *et al.* 2017).

Water Content

By adding water to dilute the DES, it is noteworthy that the physical and chemical properties of DES can be adjusted by adding a certain proportion of water (Dai *et al.* 2015). The water content also affects the performance of DES in biomass treatment. An appropriate amount of water content can improve capacity of biomass composition extraction (Vilková *et al.* 2020). Recently, Soares *et al.* (2019) stated that the water can provide 'co-solvency enhanced solubilization.' This implies that water can serve as a co-solvent in a DES. In the meantime, as for the structure of DES, both hydrophilic hydroxyl groups and non-polar structure parts are present, and these not only can ensure miscibility with water, but also they can create a dispersive driving force for biomass components.

External Conditions

Improper external conditions will limit the capacity of the DES. Temperature is the most important factor. When the temperature is rather low, the viscosity increases and results in deficiency of interaction between the reactants (Procentese *et al.* 2015; Mamilla *et al.* 2019). However a higher temperature may lead to the condensation of reactants, such as the lignin (Alvarez-Vasco *et al*. 2016), and that is also detrimental to the biomass treatment (Kohli *et al.* 2020), even reducing the bioactivity of the extracts (Hsieh *et al.* 2020; Wang *et al.* 2020a). Furthermore, the solid-liquid ratio is another important factor. When the proportion of solid is too high, the efficiency will decrease significantly (Bentley *et al.* 2020).

The Toxicity of DESs

Among the current, widely-used DESs, some of them are recognized as low toxic. They are popular, owing to the distinct advantages of biodegradability, recyclability, and almost no volatility (Hayyan *et al.* 2013; Florindo *et al.* 2019; Barbieri *et al.* 2020). When it is used as extraction agent of drugs or food, certainly, the choice of DES is more stringent. Panić *et al.* (2021) showed that when using betaine or thymol as HBA, and ethylene glycol, glucose, sucrose, or decanoic acid as the HBD, the extracts possessed desirable activity toward the growth of normal human keratinocytes. At the moment, there is no denying that some DESs are also slightly toxic (Zargar *et al.* 2022), but they are still much less toxic than some ionic liquids (Musarurwa and Tavengwa 2021). More importantly, there is also less information available to give a conclusion, which means that further study is necessary. In fact, there are many other factors affecting the properties of DESs. But the factors have up to this point remained scattered in various published literature, and there has been a lack of systematic research.

DESs – THE GREEN MEDIUM FOR BIOMASS TREATMENT AND NANOCOMPOSITES

In recent years, DESs have gained massive attention in a lot of fields (Shishov *et al.* 2020), such as biorefinery, electrochemistry, biomedical/medicine, electrochemical analysis, and preparation of functional composite materials, *etc*. Among the rest, the potential of using the DESs as a green medium in biomass treatment and transformation is vast. That is to say, DESs can react with biomass, which can lead to the transformation (Majová *et al.* 2017; Tian *et al.* 2022), fractionation (Chen and Wan 2018), separation (Loow *et al.* 2017; Kumar *et al.* 2020), and modification (Smirnov *et al.* 2020; Douard *et al.* 2021) of biomass components. The separation of the main components – lignin and cellulose has been extensively studied (Smirnov *et al.* 2020; Douard *et al.* 2021). Highly valuable but trace components, such as phenolics and anthocyanins (Cao *et al.* 2018), also have been extracted from biomass resources, by which it is feasible to obtain various extracts for direct-use and later-use. Not only that, some DES can affect the microstructure of biomass, serve as an auxiliary for the preparation of biomass nanoparticles, or control the formation of composites (Smirnov *et al.* 2020; Douard *et al.* 2021; Luo *et al.* 2022) Thus, it can be said that DESs have a myriad of promising applications in biorefinery, agriculture, analytical chemistry, food safety, and so on.

Extraction and Microextraction

The most well-known function of DESs is to extract components from biomass resources. And then, by breaking the hydrogen bond network., *etc.* between the solvents, certain components can be induced to precipitate out of the DES solution. This also provides the advantage of recycling. Some DESs are easily recovered by adding water, or with vacuum distillation (Luo *et al.* 2022; Tian *et al.* 2017; Shen *et al*. 2019). There are multifarious substances that can be dissolved in DESs, such as metals (Abbott *et al.* 2004), bioactive substances (Wagle *et al.* 2014; Gállego *et al.* 2015), and protein (Chen *et al.* 2021). It is interesting to find that when it is used to extract proteins, DESs have much higher extraction efficiency and recovery rate than water and conventional organic solvents (Nakhle *et al.* 2021). The DESs also can be used in both liquid-solid extraction and liquid-liquid extraction, especially in the analytical chemistry field (Raj 2020; Tang *et al.* 2021). DES also produces great value in liquid-phase microextraction techniques (Shishov *et al.* 2019; Li *et al.* 2020a). This part focuses on the applications of DES in biomass treatment and the mechanisms.

Lignin extraction and separation

DESs have been widely applied in biomass treatment for lignin extraction in recent years. The DESs with different properties can be used to extract lignin in different ways. In the case of DESs containing ChCl, they could selectively extract lignin via cleaving lignin-carbohydrate linkages and lignin ether bonds, as well as by the formation of hydrogen bonds with lignin (Guo *et al.* 2022). It was thought that the alkaline-DES, *e.g.* DES composed of ChCl and urea, can produce ammonia, and which can lead to the destruction of the structure of lignin (Simeonov and Afonso 2016). As for the acidic-DES, Li *et al.* (2021a) have studied the interaction of Brønsted acidic DES based on ChCl and p-toluenesulfonic acid with alkali lignin (AL) at mild temperature. By comparing the chemical structure changes and the degraded small molecule products in the regenerated lignin, they were able to propose a possible theory. They proposed an attack of protons on the α-position of the hydroxy groups in the lignin alkyl side chains(Li *et al*. 2021). Moreover, Tan and coworkers (Li *et al.* 2017) found that lignin could be extracted by DES at room temperature with an extraction efficiency as high as 91.8%.

According to Liu *et al.* (2017), the extracted lignin samples with DES have high purity (96%), and low molecular weight. In order to improve the efficiency of component separation from biomass, microwave and/or ultrasonic energy was introduced (Liu *et al.* 2017; Chen and Wan 2018; Mansur *et al.* 2019; Kohli *et al.* 2020).

For the rest, some representative research results are summarized in Table. 3. It is obvious that different DESs and means of assistance result in different effects on various raw materials.

Table 3. Summary of Typical Extraction of Lignin from Biomass Resources with DESs

No.	Feedstock	HBD	HBA	Mole ratio	Conditions	Delignification or Extraction (%)	Reference
1	Willow	Lactic acid	ChCl	10:1	20 °C, 12 h	91.8%	(Li *et al*. 2017)
2	Rice straw	Lactic acid	ChCl	5:1	60 °C, 12 h	60%	(Kumar *et al.* 2016)
3	Eucalyptus	Lactic acid	ChCl	10:1	110 °C, 6 h	80%	(Shen *et al.* 2019)
4	Sugarcane bagasse	Lactic acid	ChCl	5:1	80 °C, 12 h	50.6%	(Satlewal *et al.* 2018)
5	Corncob	Oxalic acid	ChCl	1:1	90 °C, 24 h	98.5%	(*Ma et al.* 2016)
6	Corncob	Glycerol	ChCl	2:1	150 °C, 15 h	59%	(Procentese *et al*. 2015)
7	Corncob	Ethylene glycol	ChCl	2:1	90 °C, 24 h	87.6%	(Zhang *et al.* 2016)
8	Poplar	Oxalic acid	ChCl	1:1	Microwave, 3 min	80%	(Liu *et al.* 2017)
9	*Panicum virgatum*	Ethylene glycol, PTSA	GH	1.94:0.06:1	120 °C, 6 min	82.1%	(Chen *et al.* 2019b)
10	Corncob	Lactic acid	BTMAC	2:1	140 °C, 2h	63.4%	(Guo *et al.* 2019)
11	Poplar	Glycerol, aluminum chloride hexahydrate	ChCl	1:0.28:2	120 °C, 4 h	95.46%	(Xia *et al.* 2018)
12	Corncob	Lysine	Betaine	1:1	60 °C, 5 h	49.06%	(Liang *et al.* 2020)

High value-added natural products extraction

DES is commonly regarded as an effective alternative to organic solvents (Oomen *et al.* 2020). The antioxidant capacity for the extracts and practical values of DES were also highlighted (Wang *et al.* 2020b; Redha 2021). DESs have also been adopted to extract high valuable substances from natural resources, including flavonoids, phenols, alkaloids, polysaccharides, volatile, and anthocyanins (Cui *et al.* 2015; Wei *et al.* 2015; Wang *et al.* 2017; Chanioti and Tzia 2018; Zang *et al.* 2020). In case of phenols, their antibacterial and anti-inflammatory properties have been demonstrated, so the efficient extraction has been widely studied. According to Lu and Liu (2020), the formation of 'Ch-DES/Phenolic Compounds supramolecule' appears to be the key step in such a process .

DESs have also attracted interest in the aspect of the natural trace components with high value. Li and Row (2021) developed an interesting sensitive microsphere, which highlighted the feasibility of using DES (ChCl : p-hydroxybenzoic acid =1:1) as both a functional monomer and template for the extraction of p-hydroxybenzoic acid. The extraction capacity was as high as 46.3 mg/g under the optimized conditions. In addition, multi-component extraction is also realized by DES, according to the report of Wei *et al.* (2015). It was found that DES, composed of ChCl and maltose, had a much higher extraction capacity of different polarity compounds than conventional solvents. Table 4 lists some representative examples to illustrate the versatility of the DESs.

Table 4. Some Representative Examples of High Value-added Products Extraction

Natural Product	Feedstock	DES	Mole Ratio	Solid Ratio (mL/g)	Conditions	Yield	Antioxidant Activity	Reference
Proantho-cya-nidin (PAC)	*Ginkgo biloba*	ChCl/malonic acid	1:2	10.57/1	65 °C, 53 min, water content 55% (w/w)	22.19±0.71 mg/g	A little less than methanol	(Cao *et al*. 2018)
Oleuropein, verbascoside and rutin	Olive leaf	citric acid/lactic acid	1:4	-	48.9% of water in DES for 60 sec at 13310 rpm	15.50, 5.51 0.98 mg/g reps	--	(Şahin *et a*l. 2021)
HSYA and ASYB	Safflower	L-Proline/ Malic Acid	1:1	1/0.2	50 °C,30 min, 200 W ultrasonic assisted	32.83 and 8.80 mg/g	Bioavailability is much higher	(He *et al*. 2020; Tong *et al*. 2021)
Betalains	Beet root waste	$MgCl_2 \cdot 6H_2O$/ urea	1:1 /2:1	30/1	25 °C, 3 h ultrasonic assisted	A similar content to water extracts	Betalain is of great stability	(Hernández-Aguirre *et al*. 2021)

***** HSYA: hydroxysafflor yellow A, ASYB: anhydrosafflor yellow B

Nanomaterials and Nanocomposites

In addition to extracting components from biomass (Park *et al.* 2021), DESs also play a key role in obtaining biomass derived nanomaterials and nanocomposite processing. In this part, the biomass derived nano-lignin, nanocellulose (usually used as the reinforcement), as well as the related nanocomposites developed with DESs as medium or template are reviewed concisely. As shown in Table 5, changes in structure and size of lignin/cellulose after the DES pretreatment are noted, and these will be explained in the next section.

Cellulose nanocrystals

DESs have been applied as a pretreatment for biomass transformation and application (Chen *et al.* 2019a; Elgharbawy *et al.* 2020). With the progress of the research, it was found that DES can change the properties of natural cellulose, which means that it has the potential for transformation of nanocellulose/cellulose nanocrystal (Chang *et al.* 2021). Smirnov *et al.* (2020) used DES composed of ChCl and urea; they successfully prepared cellulose nanocrystals (CNCs) with microcrystalline cellulose as the raw material. The findings revealed that a key step in this process was the hydrogen bond formation of the hydrogen bonds between the hydroxyl groups in cellulose with the carbonyl groups of urea.

Other important function came from the chloride ions destructed from the DES, which retained the crystal structure of cellulose (Iβ) and the swelling behavior of cellulose (amorphous cellulose) was the key issue for making CNCs. Dourd *et al.* (2021) reported their work on preparation of cellulose nanocrystals (CNCs) with crystallinity index of 80±1% in 35.5±2.7% yield from recycled cotton fibers from the industry paper with acidic NADES composed of ChCl and oxalic acid dihydrate in a molar ratio of 1:1. Kumar *et al.* (2016) discovered that the crystallinity index ratio was marginally decreased by 2 to 3% after the rice straw was pretreated with some methods.

To avoid causing damage to cellulose structure, Yu *et al.* (2021) applied DES composed of ChCl and oxalic acid in a molar ratio of 1:1 to swell ramie fibers for further preparation of cellulose nanofibril. Obvious differences in the crystallinity and other properties were observed. Compared with other mature processing technology, DES can cleave the hydrogen bond of natural cellulose, expand and disperse cellulose, which provided an environmentally-friendly candidate for processing of cellulose nanofibril (CNF) films.

Nano-lignin and nanocomposites

The process of lignin from biomass raw materials with DESs has already been discussed in this chapter. Moreover, DESs can also regulate the morphology and structure of lignin to prepare nano-lignin and lignin nanocomposites. Lignin nanoparticles (LNPs) are promising candidates for preparation of next-generation functional nanocomposites. Lignin nanocomposites can be prepared safely and innocuously through a simple process and used in industrial production by enrolled DESs in the process.

According to Luo *et al.* (2022), kraft lignin was dissolved completely in DES composed of ChCl and ethanolamine in ratio of 1 to 6, after 2 h at ambient temperature to conveniently prepare homogeneous spherical lignin nanoparticles with sizes ranging from 123.6 to 140.7 nm, using a solvent-antisolvent method. LNPs with sodium alginate (SA) were also integrated to prepare SA/LNPs composite bend (nano adsorbent), which presented high efficiency of 97.1% in removing methylene blue. The nano-lignin composite contained both hydrophobic groups and hydrophilic groups, which makes it possible for formation uniform hydrophilic nano-micelles in aqueous solutions. Nano-lignin with various morphologies has also been prepared. Tian *et al.* 2017) demonstrated the feasibility to obtain and high-value lignin nanoparticles with core-shell structure in uniform sizes with average particle size of 195 nm and shell thickness about 10 to 20 nm. The zeta-potential value was tested to be −37.5 mV, which indicated the high stability. The lignin nanoparticles were judged to be promising candidates for degradable nanocomposite films with PVA matrix.

Nanocomposites

The nanocomposites, which can be defined as combinations of materials having at least one external nanoscale dimension or having internal nanoscale structure, is the very important branch in material field (Ray and Salehiyan 2020). At the same time, the treatment with DESs is an effective way to prepare nanocomposites. Based on their capabilities for dissolving and modification, DESs can be used to prepare high performance and functional nanocomposites.

Liu *et al.* (2020) used microwave action to promote the DES composed of ChCl and LA with the ratio of 1 to 10. They obtained lignin-containing cellulose nanofibers (LCNFs) from the sugar cane bagasse and prepared LCNFs/ polyanionic nanocomposite film with tunable mechanical property and nice UV-resistance by changing the dosage of LCNFs. DES was able to promote the esterification lignin of nanoparticles.

As reported by Zhang *et al.* (2021), the DES was prepared, which was composed of ChCl and LA in the molar ratio of 1 to 9. Mechanical colloid milling was used to obtain esterified lignocellulose nanofibers (LCNFs) from lignocelluloses raw material, and then with a direct blending, the LCNF/polylactic acid composites were prepared. The interfacial compatibility was considerably improved to reach 120.6% higher flexural property for the as-prepared polylactide-based nanocomposites, compared with pure polylactic acid. Besides, DESs also have many other important and interesting functions. According to Marcial *et al.* (2021), an acidic-DES composed of ChCl and Oxalic acid dihydrate was applied to *in situ* prepare nanocellulose dispersions (CNCs) in the styrene/divinylbenzene emulsions and further to obtain the microporous polymer composites through free radical polymerization with addition of initiator.

The more interesting point is achieved by tuning the compositions of DES to realize various aims. For example, in order to prepare porous biomass based supercapacitors, according to Chen *et al.* (2020), the urea and the functional DES were used, the DES was obtained by mixing ChCl and $ZnCl_2$, which was taken as both soft template and nitrogen source. The urea decomposed, leading to the generation of ammonia and isocyanic acid and also the formation of nitrogen-containing groups through the substitution of aromatic hydroxy groups in lignin, which produced micropores in the material. Thus, a sustainable functionalization approach was demonstrated.

Table 5. Changes in Product Structure and Size Caused by DES Pretreatment

Feedstock			DES		Assistant Methods	Product			Reference
Structure	Size (μm)	Crystallinity Index	Species	Molar Ratio		Product	Average Dimensions/ Diameter (nm)	Crystallinity Index	
Microcrystalline cellulose	20*100	85%	ChCl: urea	1:2	-	CNCs	20 * 100 *700	80%	(Smirnov *et al.* 2020)
Cotton fibers	689*25	79%	ChCl: $C_2H_6O_6$	1:1	-	CNCs	11*257	80 ±1 %	(Douard *et al.* 2021)
Cotton fibers	-	61%	OA: betaine	1:2	Ultrasonic method	CNFs	100-200	Increased by 5% to 20%	(Deng *et al.* 2022)
Raw ramie fibers	-	-	ChCl: $C_2H_6O_6$	1:1	Ball-mailing	CNFs	15 * 530	79%	(Yu *et al.* 2021)
Kraft lignin			ChCl: ETA	1:6		LNPs	123.6-140.7	-	(Luo *et al.* 2022)
Woody biomass			LA:betaine	-	-	LNPs	195		(Tian *et al.* 2017)
Prepared lignocelluloses	-	71.04%	ChCl:LA	1:9	Colloid mill	LCNFs	Tens-few hundred nanometers	73.43%	(Zhang *et al.* 2021)
Energy cane bagasse	-	-	ChCl:LA	1:10	Microwave irradiation	LCNFs	Tens of nanometers	-	(Liu *et al.* 2020)
Corncob fragments	-	-	ChCl:AC	1:2	Enzymatic hydrolysis, *etc.*	LCNFs	60-90	77.21%	(Li *et al.* 2021)

* ETA: ethanolamine, $C_2H_6O_6$: oxalic acid dihydrate, OA: oxalic acid, LA: lactic acid, AC: acetic acid CNCs: cellulose nanocrystals, CNFs: cellulose fibrils lignin nanoparticles, LCNFs: lignin-containing cellulose nanofibers

OTHER APPLICATIONS WITH BIOMASS

Pretreatment to Improve Enzymolysis or Saccharification Efficiency

Enzymatic saccharification is a significant domain of biorefinery, which is of global interest. Saccharification is an important way to rationally utilize biomass and reduce the waste of biological resources (Guo *et al.* 2018; Wang and Lee 2021). During the pretreatment, DES can decrease the recalcitrant properties of biomass raw materials. Part of the lignin component can be removed from biomass, and the polysaccharide components, cellulose and hemicelluloses, will then be accessible (Zhang *et al.* 2016; Thi and Lee 2019; Dugoni *et al.* 2020; Xie *et al.* 2021). Moreover, several studies have shown that the acidic-DES pretreatment could enhance the cellulose reactivity, leading to improved efficiency of saccharification. Tian *et al.* (2020) studied the pretreatment of lignocellulosic raw materials with mild acidic-DESs, and the results showed that the available area and porosity of the resulting cellulose were significantly increased. Table 6 summarizes some representative reported results.

Modification of the Compositions of Biomass

It is necessary to conduct chemical modifications to meet the requirement of application of biomass derived materials in some circumstances. DES can also play a key role in the process. Many studies have shown that DES can be useful in the chemical modification of cellulose. As early as in 2005, research on the modification of cellulose with DES has been reported (Abbott *et al.* 2005) in efficient acetylation of monosaccharides and cellulose with acetic anhydride. Moreover, Li *et al.* (2020b) proposed a feasible approach to convert glucose and cellulose to levulinic acid using phosphotungstic acid as the catalyst in DES medium. The modified cellulose can also have outstanding adsorption properties, tunable hydrophilic or hydrophobic characteristics, forming hydrogels, *etc*. (Yang *et al.* 2019; Lakovaara *et al.* 2021; Long *et al.* 2021). More interestingly, DES can react with the substrates to modify their structures. The properties of lignin obtained by using different DES would be changed, including introducing functional groups (Hong *et al.* 2016), causing structural damage (Li *et al.* 2022; Tan *et al.* 2020), leading to greater reactivity (Xian *et al.* 2021), and increasing the active sites of lignin (Xiong *et al.* 2020). Some studies have even shown that chitosan or others could also be modified in DES medium (Rangel *et al.* 2020).

Some Special Functions

There are many new interesting studies on DESs in the field of biomass (Adamus *et al.* 2018). The DESs still have great potential to be disclosed in the future. Da Silva *et al.* 2021) found that DES could be used as a carrier to increase oral absorption of bioactive compounds such as anthocyanins. Ling *et al.* (2019) applied DES to mediate formation of cotton cellulose nanocrystals (DCNCs), which would provide a convenient, sensitive sensor applicable for improving colorimetric point of care protease biomarker detection. Vorobiov *et al.* (2021) prepared the electrolyte films of the chitosan/DES, which presented pretty good ion conductivity and electrochemical stability. According to the authors, the chitosan /DES electrolytes were helpful for designing a bio-based and flexible supercapacitors.

Table 6. Pretreatment for Improving the Enzymolysis Efficiency

Feedstock	Pretreatment	DES	Mole Ratio	Removal	Pretreatment Conditions	Enzymatic Digestibility	Reference
Poplar	Particles sizes of 40-60 mesh and dewaxed	ChCl/mono-ethanolamine	1:6	Hemicelluloses	140 °C, 6 h	Increased by 6.6 times	(Yang *et al.* 2021)
Wheat straw	Fibrillated with extruder	ChCl/guaiacol /$AlCl_3$	25:50:1	Hemicellulose and lignin	80-130 °C,1 h	Complete enzymatic digestibility	(Huang *et al.* 2021)
Poplar or bamboo	Fibrillated with extruder	ChCl/guaiacol /$AlCl_3$	25:50:1	Hemicellulose and lignin	80-130 °C, 1 h; After alkali washing	Near 100% hydrolysis yield	(Huang *et al.* 2021)
Poplar wood	Sawdust of 40-60 mesh	Ethylene glycol /ChCl/ $AlCl_3$	1:2:0.1	Hemicellulose and lignin	After hydrothermal and at 100 °C, 10 min microwave	The efficiency increased by about 80%	(Ma *et al.* 2021)
Radiata Pine	Particle sizes of 40-60 mesh	Benzyltrimethyl ammonium chloride/formic acid	1:2	Hemicellulose and lignin	150 °C, 120 min	Reached at 92.4%	(Xie *et al.* 2021)
Hybrid Pennisetum	Grind	ChCl/glycerol/$FeCl_3$	-	Hemicellulose and lignin	120 °C, 6 h	99.5%, six-fold higher	(Wang *et al.* 2020c)

CONCLUDING STATEMENTS

In summary, DESs are green solvents with many prominent advantages. They not only can be used as the powerful agent to extract components from biomass, but numerous DESs can also be designed and prepared aiming at different application scenarios. DESs demonstrate richness and great application potential. Herein, the applications mainly in biomass composition extraction, and derived nanomaterials have been reviewed. However, we can only provide the prelude pages in the field of DESs related works. There is still a lot of uncertainty in DESs. In the future, DESs definitely can be applied in many other new ways, and the structures and applications of DESs will also tend to be more versatile and diverse, as well as new manufacturing technologies. It should be seriously pointed out that how to realize scaling-up the application of DESs in biomass processing remains a challenge. It is worth affirming that the development of DESs has just started, but there is no doubt that the DESs are rich in terms of application potential.

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