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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Keywords: Deep eutectic solvent (DES); Biomass treatment; 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)

<table>
<thead>
<tr>
<th>Category</th>
<th>Constituent A</th>
<th>Constituent B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Imidazolium salt</td>
<td>Metal halides</td>
</tr>
<tr>
<td>2</td>
<td>ChCl</td>
<td>Hydrated metal halides</td>
</tr>
<tr>
<td>3</td>
<td>ChCl</td>
<td>Hydrogen bond donor</td>
</tr>
<tr>
<td>4</td>
<td>Metal halides</td>
<td>Hydrogen bond donor</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Hydrogen Bond Donor</th>
<th>Hydrogen Bond Acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids</strong></td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>ChCl</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>Benzyltrimethylammonium chloride</td>
</tr>
<tr>
<td>Citric acid</td>
<td>Benzyliodideammonium chloride</td>
</tr>
<tr>
<td>Malic acid</td>
<td>Dimethylammonium chloride</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>Betaine</td>
</tr>
<tr>
<td>Levulinic acid</td>
<td></td>
</tr>
<tr>
<td>P-toluenesulfonic acid</td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td></td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td>Metal salts</td>
</tr>
<tr>
<td>Glycerol</td>
<td>ZnCl₂</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>K₂CO₃</td>
</tr>
<tr>
<td>Menthol</td>
<td></td>
</tr>
<tr>
<td>Triethylene glycol</td>
<td></td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td></td>
</tr>
<tr>
<td>Imidazole</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td></td>
</tr>
</tbody>
</table>
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/K2CO3. 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 Bronsted 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

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

<table>
<thead>
<tr>
<th>Natural Product</th>
<th>Feedstock</th>
<th>DES</th>
<th>Mole Ratio</th>
<th>Solid Ratio (mL/g)</th>
<th>Conditions</th>
<th>Yield</th>
<th>Antioxidant Activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proantho-cyanidin (PAC)</td>
<td>Ginkgo biloba</td>
<td>ChCl/malonic acid</td>
<td>1:2</td>
<td>10.57/1</td>
<td>65 °C, 53 min, water content 55% (w/w)</td>
<td>22.19±0.71 mg/g</td>
<td>A little less than methanol</td>
<td>(Cao et al. 2018)</td>
</tr>
<tr>
<td>Oleuropein, verbascoside and rutin</td>
<td>Olive leaf</td>
<td>citric acid/lactic acid</td>
<td>1:4</td>
<td>-</td>
<td>48.9% of water in DES for 60 sec at 13310 rpm</td>
<td>15.50, 5.51 0.98 mg/g reps</td>
<td>--</td>
<td>(Şahin et al. 2021)</td>
</tr>
<tr>
<td>HSYA and ASYB</td>
<td>Safflower</td>
<td>L-Proline/ Malic Acid</td>
<td>1:1</td>
<td>1/0.2</td>
<td>50 °C, 30 min, 200 W ultrasonic assisted</td>
<td>32.83 and 8.80 mg/g</td>
<td>Bioavailability is much higher</td>
<td>(He et al. 2020; Tong et al. 2021)</td>
</tr>
<tr>
<td>Betalains</td>
<td>Beet root waste</td>
<td>MgCl₂·6H₂O/urea</td>
<td>1:1 /2:1</td>
<td>30/1</td>
<td>25 °C, 3 h ultrasonic assisted</td>
<td>A similar content to water extracts</td>
<td>Betalain is of great stability</td>
<td>(Hernández-Aguirre et al. 2021)</td>
</tr>
</tbody>
</table>

* 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 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/polyactic 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 ZnCl₂, 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

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>DES</th>
<th>Assistant Methods</th>
<th>Product</th>
<th>Average Dimensions/Diameter (nm)</th>
<th>Crystallinity Index</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose</td>
<td>ChCl: urea 1:2</td>
<td>-</td>
<td>CNCs</td>
<td>20 * 100 * 700</td>
<td>80%</td>
<td>(Smirnov et al. 2020)</td>
</tr>
<tr>
<td>Cotton fibers</td>
<td>ChCl: C₂H₆O₆ 1:1</td>
<td>-</td>
<td>CNCs</td>
<td>11*257</td>
<td>80 ±1%</td>
<td>(Douard et al. 2021)</td>
</tr>
<tr>
<td>Cotton fibers</td>
<td>OA: betaine 1:2</td>
<td>Ultrasonic method</td>
<td>CNFs</td>
<td>100-200</td>
<td>Increased by 5% to 20%</td>
<td>(Deng et al. 2022)</td>
</tr>
<tr>
<td>Raw ramie fibers</td>
<td>ChCl: C₂H₆O₆ 1:1</td>
<td>Ball-mailing</td>
<td>CNFs</td>
<td>15 * 530</td>
<td>79%</td>
<td>(Yu et al. 2021)</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>ChCl: ETA 1:6</td>
<td>-</td>
<td>LNPs</td>
<td>123.6-140.7</td>
<td>-</td>
<td>(Luo et al. 2022)</td>
</tr>
<tr>
<td>Woody biomass</td>
<td>LA: betaine -</td>
<td>-</td>
<td>LNPs</td>
<td>195</td>
<td></td>
<td>(Tian et al. 2017)</td>
</tr>
<tr>
<td>Prepared lignocelluloses</td>
<td>ChCl:LA 1:9</td>
<td>Colloid mill</td>
<td>LCNFs</td>
<td>Tens-few hundred nanometers</td>
<td>73.43%</td>
<td>(Zhang et al. 2021)</td>
</tr>
<tr>
<td>Energy cane bagasse</td>
<td>ChCl:LA 1:10</td>
<td>Microwave irradiation</td>
<td>LCNFs</td>
<td>Tens of nanometers</td>
<td>-</td>
<td>(Liu et al. 2020)</td>
</tr>
<tr>
<td>Corncob fragments</td>
<td>ChCl:AC 1:2</td>
<td>Enzymatic hydrolysis, etc.</td>
<td>LCNFs</td>
<td>60-90</td>
<td>77.21%</td>
<td>(Li et al. 2021)</td>
</tr>
</tbody>
</table>

* ETA: ethanolamine, C₂H₆O₆: 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

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Pretreatment</th>
<th>DES</th>
<th>Mole Ratio</th>
<th>Removal</th>
<th>Pretreatment Conditions</th>
<th>Enzymatic Digestibility</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poplar</td>
<td>Particles sizes of 40-60 mesh and dewaxed</td>
<td>ChCl/mono-ethanolamine</td>
<td>1:6</td>
<td>Hemicelluloses</td>
<td>140 °C, 6 h</td>
<td>Increased by 6.6 times</td>
<td>(Yang et al. 2021)</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>Fibrillated with extruder</td>
<td>ChCl/guaiacol/AlCl₃</td>
<td>25:50:1</td>
<td>Hemicellulose and lignin</td>
<td>80-130 °C, 1 h</td>
<td>Complete enzymatic digestibility</td>
<td>(Huang et al. 2021)</td>
</tr>
<tr>
<td>Poplar or bamboo</td>
<td>Fibrillated with extruder</td>
<td>ChCl/guaiacol/AlCl₃</td>
<td>25:50:1</td>
<td>Hemicellulose and lignin</td>
<td>80-130 °C, 1 h; After alkali washing</td>
<td>Near 100% hydrolysis yield</td>
<td>(Huang et al. 2021)</td>
</tr>
<tr>
<td>Poplar wood</td>
<td>Sawdust of 40-60 mesh</td>
<td>Ethylene glycol/ChCl/AlCl₃</td>
<td>1:2:0.1</td>
<td>Hemicellulose and lignin</td>
<td>After hydrothermal and at 100 °C, 10 min microwave</td>
<td>The efficiency increased by about 80%</td>
<td>(Ma et al. 2021)</td>
</tr>
<tr>
<td>Radiata Pine</td>
<td>Particle sizes of 40-60 mesh</td>
<td>Benzy1trimethyl ammonium chloride/formic acid</td>
<td>1:2</td>
<td>Hemicellulose and lignin</td>
<td>150 °C, 120 min</td>
<td>Reached at 92.4%</td>
<td>(Xie et al. 2021)</td>
</tr>
<tr>
<td>Hybrid Pennisetum</td>
<td>Grind</td>
<td>ChCl/glycerol/FeCl₃</td>
<td>-</td>
<td>Hemicellulose and lignin</td>
<td>120 °C, 6 h</td>
<td>99.5%, six-fold higher</td>
<td>(Wang et al. 2020c)</td>
</tr>
</tbody>
</table>
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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