Editorial Corner

Deep Eutectic Solvent as a Tailor-made Chemical for Pretreatment in a Lignocellulose Biorefinery

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The textile industry casts a long shadow on climate change, contributing roughly 10% of global carbon emissions. Biogenic raw materials offer a promising avenue for sustainable textile production, with lignocellulose emerging as a frontrunner due to its abundance and cellulose content. However, unlocking the textile potential of lignocellulose hinges on effective pretreatment processes [1]. Ideally, such processes should be environmentally benign and economically viable, while concurrently preserving the structural integrity and value of all major biopolymers (cellulose, hemicellulose, and lignin). Achieving this trifecta of sustainability, affordability, and complete biomass valorization presents a captivating challenge for researchers and industry alike.

Deep Eutectic Solvents (DES) offer a green solution to the lignocellulose recalcitrance problem; the components of DES are generally biodegradable, it is easy to synthesize, it has a better cellulose yield, and it has the potential to completely valorize lignocellulose [2]. DES is a homogenous solution of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). The resulting solution has a lower melting point than either of its components. The lower melting point stems from the charge delocalization due to the rearrangement of hydrogen bonds [3]. DES has the general formula of $Cat^{+}X^{-}zY$, where Cat+ is a cation, which is generally a quaternary ammonium ion, X^{-} is a Lewis Base, Y is a Bronsted or Lewis acid, and z indicates the number of molecules that interact with the anion [4]. The $Cat^{+}X^{-}$ is the HBA and Y is the HBD [5]. Based on the components of HBA and HBD, DESs are classified into four types.

Among all DESs, Type III DES is the most common type used for lignocellulose pretreatment [6]. Type III DES consists of quaternary ammonium salt and HBD. Type III DES is further divided into subtypes based on the HBD employed; acid, polyol, amine, or amide. The different HBDs are used in combination with choline chloride as the HBA [2]. Acid-based DES uses organic acids such as oxalic acid, lactic acid, and formic acid as HBD. The acid-based DES has a lower pKa, hence better hydrogen bond acidity and, consequently better lignin removal [7]. The polyol-based DES employs polyols such as glycerol, ethylene glycol as HBD. The polyol-based DES has an inferior lignin removal relative to acid-based DES due to higher pKa but offers the advantage of lower corrosivity, and better sugar extraction [5]. Amine or amide-based DES are also available; however, they are not widely researched due to their low pretreatment efficiency [8]. Ternary component

DES is yet another and more recent class of DES. It consists of three components; allowing the tunability of DES to adjust to the type of biomass [9]. The third component provides an additional advantage to the binary component DES, for example, the lignin preservation ability of a binary component DES is improved by the addition of polyol, making lignin easy to valorize [9].

The mechanism of DES pretreatment entails disrupting the intermolecular bonding within lignocellulose. The Kamlet Taft parameters (α, β and π^*) determine the properties of the DES. α represents the acidity of the H-bond, β represents the basicity and π^* represents the polarizability of the solvent [5]. Higher α indicates a better proton donating ability, while higher β means a better hydrogen bond accepting ability. The delignification reactions (ether and ester bond cleavage) depend on the proton donating ability of the solvent [10]. Furthermore, the hydrogen bonds between lignin and cellulose are disrupted by a solvent with higher hydrogen bonding acceptance. Therefore, higher α and β are required for better lignin extraction [11]. DES with lower pKa exhibits higher α hence a higher delignification potential. On one hand, the α and β parameters contribute to the cleavage of bonds, π^* helps maintain the quality of lignin; the higher the polarizability, the higher the stability of the cleaved lignin bond, hence preventing the degradation (condensation) of lignin [9].

DES has an advantage over other conventional pretreatment methods in that it has the potential to valorize lignin along with cellulose [12]. The protected lignin present in the liquid phase can be extracted via an extractant. Furthermore, the DES can be recycled using distillation, improving the process sustainability [2]. The number of recycles is, however, limited. It is shown that DES maintains its performance up to 5 cycles only [5]. The integration of DES with other pretreatment techniques can significantly improve its performance. The combination of hydrothermal pretreatment with DES leads to better cellulose quality; Hydrothermal pretreatment removes hemicellulose effectively, and DES offers better delignification [13]. Using microwave to heat the DES system reduces the heating time, as well as the reaction time; microwave increases the polarity of DES consequently increasing the rate of fractionation. Coupling DES with ultrasonication improves fractionation by providing a higher biomass surface area to DES i.e., ultrasonic waves rupture biomass by cavitation [14]. The integrated techniques show better performance, but these processes should be optimized for energy input and should be compared with the energy input of the conventional DES pretreatment method.

The structure of lignocellulose is diverse, requiring a varied selection of HBA and HBD that align with the specific characteristics of the biomass. Computational techniques, such as machine learning or dynamic simulations, are essential due to the vast array of potential combinations of HBA and HBD [15]. Using these advanced methods not only saves valuable time and resources but also ensures a more precise and tailored approach to meet the demands of pretreatment processes. DES stands out as a crucial and promising technology for lignocellulosic biomass pretreatment. With biodegradable components, easy synthesis, and superior cellulose yield, DES offers an environmentally friendly solution. Despite limitations, such as limited recyclability, DES's unique ability to valorize both lignin and cellulose positions it as a superior alternative to conventional pretreatment methods. Integration with other techniques shows promise, with careful optimization needed. In essence, DES technology, with its positive attributes and ongoing advancements, presents a robust avenue for the sustainable evolution of lignocellulosic biomass processing.

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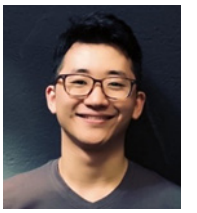

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