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Lignin conversion into aromatic compounds with deep eutectic solvents and a new proposal for downstream processing

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PURPOSE OF THE ABSTRACT

The implementation of a bioeconomy strategy as sustainable alternative to polluting fossil-based activity has been continuously stimulated by European Union in the last years to ensure the existing and future needs of society [1]. In this context, the use and processing of renewable raw materials like biomass as source of energy, fuels, materials and chemicals has been tentatively addressed. As an example, pulp and paper industries have been adopting this multiple processing approach to achieve higher sustainability in wood processing activity, where the valorization of the by-product lignin into value added products is a clear target, instead of its current use as low value fuel for energy production [2]. Besides the ambitioned valorization of lignin, the development of sustainable technologies to deliver new lignin-based products within a benefic economic and environmental framework is of utmost importance.

In this work, deep eutectic solvents (DESs) were investigated as sustainable media for lignin dissolution and depolymerization into value added aromatic compounds. The ability for lignin dissolution of eleven DES based on cholinium chloride ([Ch]Cl) as hydrogen bond acceptor (HBA) combined with alcohols or carboxylic acids as hydrogen bond donors (HBDs) was evaluated in the first place [3]. The obtained results showed that solvent HBD play an important role in lignin dissolution, and the efficiency is governed by its chemical nature (alcohol or carboxylic), chain length, and molar ratio to HBA. Among examined DES, [Ch]Cl:HEXA (1,6-hexanediol) and [Ch]Cl:MaleA (maleic acid) were the best solvents, allowing for 32.99 and 34.97 wt % lignin solubility at 40 °C, respectively. On the other hand, the addition of water negatively affected the lignin solvation power of DES, but at different degrees. Moreover, thermal treatments of lignin at 120 °C showed that alcohol-based DESs were capable of maintaining the lignin chemical structure, while carboxylic acid-based DESs enabled chemical modifications, especially on the disruption of ?-O-4 ether bonds as demonstrated in 2D NMR HSQC data depicted Figure 1 [3].

Due to its reactivity with lignin, [Ch]Cl:OxaA was tested as dual role solvent-catalyst to breakdown Organosolv lignin (OL) and Kraft lignin (KL) into value-added aromatic compounds, either in absence or presence of co-catalysts (H2SO4 and H2O2). The obtained data showed that approximately ¼ of the initial lignin was converted into depolymerization products after breakdown of the two technical lignins. Furthermore, the profile of depolymerization products was distinct between examined lignins as well as between acidic ([Ch]Cl:Oxa and

[Ch]Cl:Oxa/H2SO4) and acidic oxidative treatments ([Ch]Cl:Oxa/H2O2). The formation of syringol and acetosyringone was favored in acidic treatments of KL, while vanillic and syringic acids were the main products in analogous treatments of OL. On the other hand, the presence of H2O2 in DES promoted substitutions in the aromatic ring of lignin monomers forming chlorinated compounds.

Additionally, a tentative downstream processing was developed for the separation of lignin monomers based on polymer-polymer type aqueous biphasic system (ABS) coupled with Centrifugal Partition Chromatography (CPC). Vanillic acid presented distinct physicochemical characteristics from other lignin monomers, enabling a selective separation. Further processing by combining ultrafiltration (UF) and solid phase separation (SPE) was approached to isolate vanillic acid and to recover phase-forming constituents as proof of concept. Up to 82.1 % recovery yield of initial vanillic acid and maximum purity of 95.6 % was achieved with this downstream processing.

FIGURES

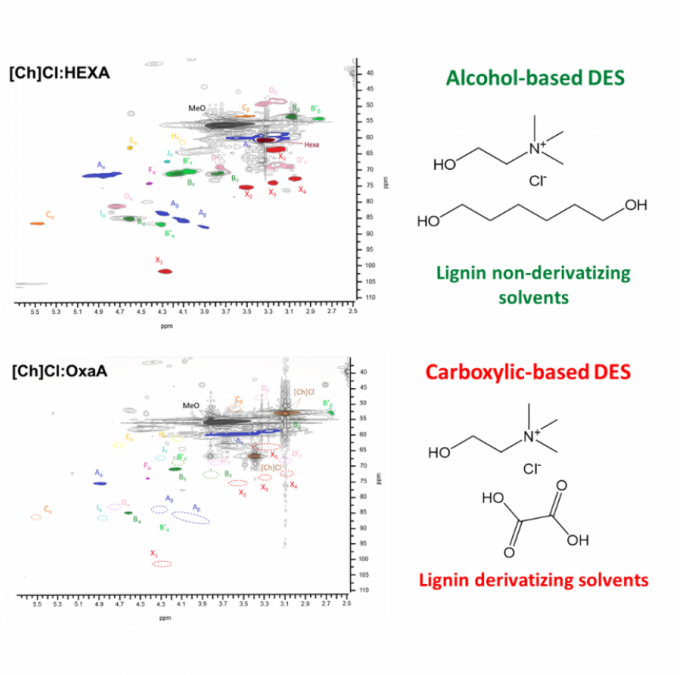

FIGURE 1

2D NMR spectra of lignin samples

HSQC of Kraft lignin after thermal treatment (120 °C, 6 h) with alcohol-based DES ([Ch]Cl:HEXA) and carboxylic acid-based DES ([Ch]Cl:HEXA)

FIGURE 2

KEYWORDS

lignin depolymerization | aromatic compounds | downstream processing | sustainable

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