Kraft Lignin Solubility and Its Chemical Modification in Deep Eutectic Solvents

Filipe H. B. Sosa, Dinis O. Abranches, André M. da Costa Lopes,* João A. P. Coutinho,*
and Mariana C. da Costa

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ABSTRACT: Lignin stands as a promising raw material to produce commodities and specialty chemicals, yet its poor solubility remains a big challenge. Recently, deep eutectic solvents (DES) have been proposed as sustainable solvents with high potential to dissolve and valorize lignin. In the present study, the ability of DES based on cholinium chloride ([Ch]Cl) combined with alcohols and carboxylic acids as hydrogen bond donors (HBDs) to dissolve kraft lignin and to change its chemical structure was examined. The influence of the chemical nature of HBDs, water content, and HBD:hydrogen bond acceptor (HBA) molar ratio on the solubility of kraft lignin in DES was studied (313.15 K). The kraft lignin solubility was enhanced by increasing both the HBD's carbon chain length and the molar ratio, with [Ch]Cl:HEXA (1,6-hexanediol) and [Ch]Cl:MaleA (maleic acid) being the best studied solvents for kraft lignin dissolution, while the addition of water was a negative factor. The thermal treatments (393.15 K) of kraft lignin show that carboxylic acid-based DES promote chemical modifications to kraft lignin, including the disruption of several C−O covalent type bonds (*e.g.*, β-O-4, α-O-4 and α-O-α), while alcohol-based DES were found to be nonderivatizing solvents maintaining the lignin chemical structure. These results show the versatility of DES, which, depending on their chemical nature, may offer distinct strategies for lignin valorization.

KEYWORDS: *deep eutectic solvents, kraft lignin, solubility, hydrotropy, depolymerization, nonderivatization*
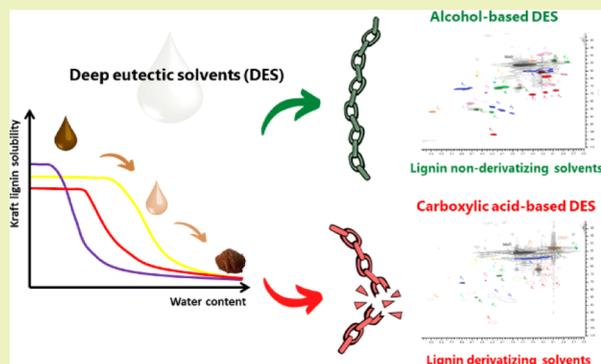
INTRODUCTION

Lignin is considered the second most abundant natural macromolecule on the planet (after cellulose) and represents an important source of aromatic compounds.[1] The lignin chemical structure is characterized by randomly linked interunit bonds, such as ether (*e.g.*, β-O-4, α-O-4, and 4-O-5) and carbon−carbon (*e.g.*, 5-5', β-5, β-1, and β−β) linkages, established between three phenylpropanoid units: *p*-coumaryl, coniferyl, and sinapyl alcohols. This allows lignin to present an amorphous and rather complex structure, acting as a glue to give hardness to plant biomass and to protect from microbial attacks.[1]

One of the most abundant sources of lignin comes from the activity of pulp and paper companies. The production of cellulose pulp from wood is generally performed by delignification processes, the kraft process being one of the most applied in the industry, producing kraft lignin as a byproduct. In the kraft process, wood is treated with a solution of sodium hydroxide and sodium sulfide at a relatively high temperature (170 °C) enabling delignification. The cleavage of α-O-4 and β-O-4 bonds is favored, while resinol substructures (β−β) are highly conserved in the kraft lignin structure.[2] Indeed, the ratio between resinol and β-O-4 substructures in
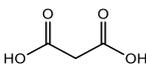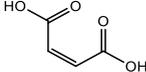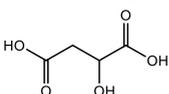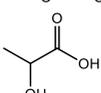
this lignin was found higher than that reported for other technical lignins.[3,4] Furthermore, recondensation reactions also occur leading to the formation of other C−C bonds increasing the recalcitrance of this technical lignin.[5,6] In addition, thiol groups are incorporated into lignin in this process, and undesirable impurities such as sulfurous compounds or carbohydrates are present in lignin.[7]

Traditionally, kraft lignin is used as feedstock in boilers, where it is burnt to generate energy to the factory grid.[8] However, pulp and paper companies have shown increasing interest for the valorization of this byproduct as a precursor to produce added value chemicals and materials[9] rather than its combustion. However, kraft lignin is poorly soluble in water, while lack of cheap, efficient, and environmentally safe solvents for lignin dissolution prevents its successful valorization. In this context, a promising green and eco-friendly approach for lignin

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Table 1. List of DES Used in This Study

DES	HBD's chemical structures	Molar Ratio (HBA:HBD)
Alcohols		
[Ch]Cl:EGLY		2:1; 1:1; 1:2
[Ch]Cl:GLY		2:1; 1:1; 1:2
[Ch]Cl:PROP		1:2
[Ch]Cl:BUT		1:2
[Ch]Cl:PENT		1:2
[Ch]Cl:HEXA		1:1; 1:2
Carboxylic acids		
[Ch]Cl:OxaA		2:1; 1:1; 1:2
[Ch]Cl:MaloA		2:1; 1:1; 1:2
[Ch]Cl:MaleA		2:1; 1:1
[Ch]Cl:MaliA		1:1; 1:2
[Ch]Cl:LacA[a]		2:1; 1:1; 1:2
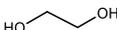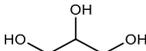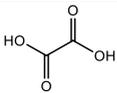
[a]Used in this study as reference.

dissolution relies on the deployment of a class of solvents known as deep eutectic solvents (DES).

DES, first introduced by Abbott *et al.*,[10] are mixtures of two or more components capable of establishing hydrogen bond interactions and enabling a significant negative deviation of the mixture's melting temperature from that predicted for an ideal mixture.[11] This depression in melting temperature makes some of the existing DES to be liquid at room temperature and further used as solvents in a plethora of applications. Generally, two components are used in their preparation, including a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). Quaternary ammonium salts, mostly cholinium chloride ([Ch]Cl), stand as most used HBA components because of their low cost, low toxicity, biodegradability, and easy preparation.[12] Substances such as urea, alcohols,[13] fatty alcohols or fatty acids,[14] sugar, and carboxylic acids[15] have been often applied as HBDs. Therefore, DES can be considered as an alternative to conventional organic solvents, which (part of them) are generally volatile, flammable, explosive, and toxic.[16]

There has been an increasing number of studies showing the successful application of DES as powerful solvents for biomass delignification, whereas acid-based DES have been highlighted for their ability to disrupt β-O-4 in the lignin structure.[17−19] Alvarez-Vasquez *et al.* revealed that [Ch]Cl:lactic acid(LacA)

is highly selective for the cleavage of these ether bonds in lignin structure, forming Hibbert ketones, similar to well-known lignin acidolysis processes (*e.g.*, HCl).[17] However, it was recently shown that the halide anion of [Ch]Cl may play an important role as nucleophile by substituting lignin hydroxyl groups nearby ether linkages. This allows the formation of stable intermediates that precede and favor the ether bond cleavage.[20]

However, the study of lignin dissolution in DES, especially technical lignins from well-established delignification processes (*e.g.*, kraft pulping), toward their further valorization is still barely examined.[21,22] Francisco *et al.*[23] investigated a wide range of DES to dissolve low sulfonated kraft lignin and cellulose. The authors used carboxylic acids as HBDs, while alanine, betaine, [Ch]Cl, glycine, histidine, proline, and nicotinic acid were chosen as HBAs. Most of the examined DES showed high lignin solubility, but little or negligible solubility of cellulose, demonstrating the high selectivity of these solvents for lignin dissolution. Among the tested DES, betaine:malic acid (1:3) exhibited the best performance for lignin dissolution. In another work, Lynam *et al.*[24] studied the dissolution of kraft lignin in several DES, which demonstrated the capacity to dissolve between 9 and 14% (wt_{lignin}/wt_{DES}) at 333.15 K. [Ch]Cl:formic acid (1:2) was found the best HBA:HBD combination for kraft lignin dissolution.[24]

The use of DES aqueous systems has also arisen the interest to solubilize technical lignins. Hou et al.[25] observed that small amounts of water (5 wt %) negatively affected lignin solubility in [Ch]Cl:urea (1:2), while an opposite trend was highlighted for proline:malic acid (3:1) and [Ch]Cl:oxalic acid (2:1) at the same water content. For instance, adding 5 wt % water content to proline:malic acid (3:1) increased the solubility of kraft lignin from 2.7 to 9.4 wt %. The differences observed in the effect of water on lignin solubility by those DES were suggested to be dependent on DES chemical nature (basicity vs acidity). The addition of water was beneficial for acid-based DES rather than nonacidic [Ch]Cl:urea (1:2). In other study, Yiin et al.[26] also observed that lignin solubility in malic acid:sucrose:water systems was improved from 6.38 to 9.16 wt % with increasing molar ratio of water from 1:1:1 to 1:1:10.[25] A more detailed study upon lignin dissolution in DES aqueous solutions was performed by Soares et al.[27,28] Their work showed that some DES act as hydrotropes enabling lignin dissolution in aqueous media.[27] For example, urea:propionic acid (1:2) at 50 wt % water content dissolved 3 times more kraft lignin than neat DES. The hydrotropic mechanism was confirmed by dynamic light scattering. The same authors investigated the ability of DES to act as hydrotropes or cosolvents in aqueous solutions using lignin model compounds, kraft and organosolv lignins.[28] The hydrotropic mechanism led to a notable increase in kraft lignin solubility of urea:propionic acid (1:2) aqueous solution by about 228-fold of the solubility in water, while the cosolvency provided by tetrabutylphosphonium chloride/ethylene glycol (EGLY) allowed an improvement of about 163-fold. In the latter, water revealed to be a negative factor in lignin dissolution.[28]

Few studies have engaged efforts to study the fundamentals of the lignin dissolution mechanism in DES, while the chemical modifications in lignin structure during dissolution have been barely tackled. Therefore, the present study aimed at understanding the solubility of kraft lignin in different DES and their aqueous solutions in the first place at 313.15 K and further evaluating the chemical modifications in kraft lignin structure at high temperature (393.15 K) to ascertain a successful strategy for the valorization of this technical lignin assisted by DES.

■ MATERIALS AND METHODS

Chemicals. The preparation of DES studied in this work involved combinations of [Ch]Cl with the following compounds: glycerol (GLY), EGLY, 1,3-propanediol (PROP), 1,4-butanediol (BUT), 1,5-pentanediol (PENT), 1,6-hexanediol (HEXA), as well as lactic (LacA), oxalic (OxaA), malic (MaliA), malonic (MaloA), and maleic (MaleA) acids. All chemicals were used as received, and their water contents were measured using a Metrohm 831 Karl Fischer coulometric titrator (Table S1 in Supporting Information). Their chemical structures and HBA:HBD molar ratios studied in this work are depicted in Table 1. Kraft lignin from *Eucalyptus urograndis* was directly supplied by Suzano (Brazil). It was isolated employing carbon dioxide (CO_2) to the industrial black liquor, resulting in a kraft lignin solid sample composed of 95% lignin, 2% xylans, and 3% ash contents with Mw = 1520 g mol^{-1}, Mn = 1345 g mol^{-1}, and polydispersity index = 1.13.

DES Preparation. Specific molar amounts of [Ch]Cl and corresponding HBD (see Table 1) were placed in sealed glass vials with a stir bar and heated in a paraffin bath at 333.15 ± 0.01 K with constant stirring until a clear liquid was achieved.[15] The water content in prepared DES was measured using a Metrohm 831 Karl Fischer coulometer, and the obtained values were considered for the preparation of DES aqueous solutions (5, 15, 25, 35, 45, 50, and 75

wt % water contents). These aqueous solutions were prepared by diluting the neat DES in distilled water.

Lignin Solubility Assays. An excess of kraft lignin was added to 2.00 ± 0.01 g of DES (or its aqueous solution) in glass flasks with a magnetic stirring bar. The vials were sealed and placed in an aluminum block holder that was transferred to a heating plate temperature control (PT100) magnetic stirrer (series H03D from LBX Instruments). Solubility tests were performed at 313.15 K under constant stirring at 150−200 rpm. The samples were kept under agitation until reaching saturation state and then filtered using polytetrafluoroethylene filters (0.45 μm pore size) to remove undissolved solid lignin. The saturated liquid phase was diluted with dimethyl sulfoxide (DMSO, 99.98%, Fischer Scientific, EUA), and lignin concentration was quantified at a wavelength of 280 nm by UV spectroscopy (Synergy HTX Multi-Mode Reader from BioTek Instruments). Lignin calibration curves using known amounts of the same kraft lignin sample dissolved in DMSO were obtained (at 280 nm wavelength) for the determination of lignin solubility (Figure S1 shows an example). All solubility tests were performed in duplicate. The kraft lignin solubility was calculated by the following equation

$$\text{lignin wt\%} = \frac{m_{\text{lignin}}(g)}{m_{\text{DES}}(g)} \times 100 \tag{1}$$

Thermal Treatment of Kraft Lignin. A sample of kraft lignin (600 mg) was added to 3.00 ± 0.01 g of DES (5 wt % water content) in a glass tube reactor with a stirring bar. The tubes were sealed and placed in a Radleys Carousel Tech (Radleys, United Kingdom) for 6 h at 393.15 K and kept under agitation. After treatment, 15 mL of cold distilled water (283.15 K) was added to the resulting solution and mixed in a vortex stirrer (VWR international Reax Top) to promote lignin precipitation. The solution was then introduced into an ice bath to increase the precipitation efficiency. The precipitated lignin was filtered by vacuum and washed with distilled water (200 mL) to ensure DES removal. The obtained solid was oven-dried at 323.15 K to a constant weight, and the amount of precipitated lignin was determined gravimetrically. A blank experiment using water was performed at the same conditions.

Fourier Transform Infrared with Attenuated Total Reflection Analysis. The Fourier transform infrared (FTIR) spectra of lignin samples were recorded on a PerkinElmer Spectrum BX spectrometer equipped with a horizontal Golden Gate attenuated total reflection (ATR) cell and a diamond crystal. A total of 32 scans were acquired in absorbance units for each sample with a resolution of 4 cm^{-1}, and the wavenumber ranges between 4000 and 400 cm^{-1}.

Two-Dimensional Heteronuclear Single-Quantum Correlation Nuclear Magnetic Resonance Spectroscopy. Approximately, 60 mg of lignin sample was carefully mixed in 500 μL of DMSO-d$_6$ with trimethylsilane as the internal reference. After complete dissolution, the resulting solution was transferred to an NMR tube. Two-dimensional ^{1}H−^{13}C chemical shift correlation heteronuclear single-quantum correlation nuclear magnetic resonance (HSQC NMR) spectra were acquired on a Bruker AVANCE 500 MHz NMR spectrometer (Bruker, Billerica, MA) equipped with an inverse gradient 5 mm TXI ^{1}H/^{13}C/^{15}N cryoprobe, using the Bruker-supplied pulse sequence "hsqcetgp" with 2D H-1/X correlation via double inept transfer (trim pulses), Echo/Antiecho-TPPI gradient selection for phase sensitivity improvement, and decoupling during acquisition. The chemical shifts were calibrated with respect to the DMSO solvent peaks (2.49 ppm for residual proton and 39.5 ppm for 13C). All experiments were carried out at 298.15 K with the following parameters: spectral width of 11 ppm in the F2 (^{1}H) dimension and 165 ppm in the F1 (^{13}C) dimension with 1024 data points, 194 scans, and recycle delay of 1.5 s.

Thermal Gravimetric Analysis. Thermogravimetric analyses (TGAs) were carried out in a differential thermogravimetric analyzer (TGA-50 Shimadzu). Approximately, 5 mg of lignin sample was placed in an aluminum pan and further analyzed under a nitrogen gas blanket using a flow rate of 50 mL min^{-1}. The samples were heated at a rate of 10 °C min^{-1} with a temperature range of 30−700 °C.

Elemental Analysis. The elemental analysis (C, H, N, and S) of lignin samples was performed in an elemental analyzer, LECO TruSpec series 630 (Michigan, US). The oxygen content was determined by the difference.

Gas Chromatography—Mass Spectrometry. The liquid phase obtained after kraft lignin thermal treatment with Ch[Cl]:OxaA was prior extracted with dichloromethane (DCM). The extraction with DCM was repeated two times, and the organic phase was collected in the same vial. The organic solvent was evaporated in a centrifugal vacuum concentrator (MiVac, US), and the resulting solid extract was redissolved in DCM to give a concentration of approximately 20 mg· L^{-1}. The sample was then analyzed by a Shimadzu QP2010 Ultra gas chromatograph-mass spectrometer equipped with an AOC-20i autosampler and a high-performance quadrupole mass filter. A DB-5 ms (30 m long, 0.25 mm i.d. and 0.25 μm film thickness) column with helium as the carrier gas (40 cm s^{-1}) was used for product separation. The chromatographic conditions used were as follows: isothermal at 80 °C for 5 min, ramped from 80 to 250 °C (8 °C min^{-1}) and ramped from 250 to 300 °C (4 °C min^{-1}) and then isothermal at 300 °C for 5 min; injector temperature of 320 °C; and split ratio equal to 1:10. The mass spectrometer was operated in the electron impact mode with an electron impact energy of 70 eV, and data was collected at a rate of 1 scan s^{-1} over a range of m·z^{-1} 50−1000. The ion source was kept at 200 °C and the interface temperature at 300 °C. Chromatographic peaks were identified by comparing their retention times and their mass spectra with the equipment mass spectral library (NIST14s MS Library Database or WILEY229 MS Library Database).

■ RESULTS AND DISCUSSION

Effect of the HBD on Kraft Lignin Dissolution. The importance of the HBD component in DES to dissolve lignin was first evaluated. DES composed of alcohols and carboxylic acids were examined for kraft lignin dissolution at 313.15 K, and the solubility values are presented in Figure 1 (also in Table S2 in the Supporting Information).

According to the obtained results, the ability of alcohol-based DES to dissolve kraft lignin can be ordered as follows: [Ch]Cl:HEXA > [Ch]Cl:EGLY > [Ch]Cl:PENT > [Ch]-Cl:GLY > [Ch]Cl:BUT > [Ch]Cl:PROP. Among the examined alcohol-based DES, [Ch]Cl:HEXA showed the
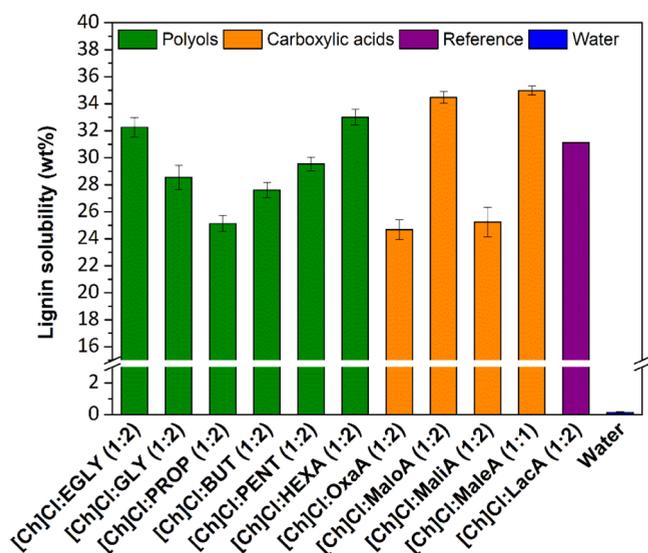

Figure 1. Solubility of kraft lignin in DES at 313.15 K. All examined DES were tested at 5 wt % water content, with the exception of [Ch]Cl:MaleA (10 wt % water content). Since a clear liquid mixture of [Ch]Cl:MaleA (1:2) is not formed at 313.15 K, a lignin solubility curve for this system was produced at molar ratio 1:1.

best performance for lignin dissolution, reaching a value of 32.99 ± 0.58 wt % lignin solubility at 313.15 K. Furthermore, a crescent trend in lignin solubility with the increase of the carbon chain length of the alcohol was observed. This is pronounced between [Ch]Cl:PROP and [Ch]Cl:HEXA (C3 to C6), but an exception was observed for EGLY-based DES, which presented a higher lignin solubility than PROP, BUT, and PENT counterparts. In the case of [Ch]Cl:EGLY, the smaller size of the HBD may favor the interaction with lignin, improving its solubility. However, despite the fact that [Ch]Cl:HEXA and [Ch]Cl:EGLY showed similar values of kraft lignin solubility, the dissolution mechanism may differ between these two DES (this is explored in the next subsection). Furthermore, the presence of an extra hydroxyl group in the alcohol carbon chain allowed an enhancement in lignin solubility ([Ch]Cl:PROP vs [Ch]Cl:GLY). Contrasting both C3 chain length PROP and GLY, the latter's extra hydroxyl group allows an additional site to establish hydrogen-bonding interactions with the kraft lignin functional groups (hydroxyl, carbonyl, and carboxylic), enhancing its solubility.[29,30] Although the influence of HBD hydroxyl groups on DES interactions with lignin has not been extensively studied, it was pointed out as one the factors favoring lignin extraction from biomass, such as oil palm empty fruit bunch.[31]

Regarding the carboxylic acid-based DES, the capacity of dissolving kraft lignin follows this order: [Ch]Cl:MaleA > [Ch]Cl:MaloA > [Ch]Cl:LacA > [Ch]Cl:MaliA > [Ch]-Cl:OxaA. The best carboxylic acid-based DES was [Ch]-Cl:MaleA by attaining 34.97 ± 0.33 wt % lignin solubility at 313.15 K. When contrasting the lignin solubility in [Ch]-Cl:OxaA (C2), [Ch]Cl:MaloA (C3), and [Ch]Cl:MaleA (C4), the increasing number of carbons in the carboxylic acid structure favored lignin dissolution,[32] which is a similar finding to that observed for alcohol-based DES. Nevertheless, when comparing alcohol-based HBDs and carboxylic acid-based HBDs with equal chain length (C3 and C4), lignin solubility seems to be favored with carboxylic acids to the detriment of hydroxyl groups. An exception was observed between the smallest size HBDs, EGLY and OxaA, both structured by two carbons. Furthermore, an opposite behavior to alcohol-based DES was also observed with the additional hydroxyl group in MaliA reducing its ability for lignin dissolution in contrast to its counterpart MaleA. In the case of MaliA structure, the additional hydroxyl group may increase the steric hindrance between HBD and lignin interaction, an opposite behavior of the extra hydroxyl group in GLY structure discussed above. Regarding MaleA, its double bond may contribute positively to the solvent interaction with lignin through π−π interactions.[31,33,34]

For both DES families studied in this work, a high capacity to solubilize kraft lignin was always achieved (>20 wt % lignin solubility). For instance, [Ch]Cl:HEXA and [Ch]Cl:MaleA led to an increment in lignin solubility of around 1.16-fold and 1.23-fold in contrast to one of the most broadly used DES, [Ch]Cl:LacA, respectively. The enhanced lignin solubility in DES is much more evident when compared with pure water: 226-fold and 239-fold for [Ch]Cl:HEXA and [Ch]Cl:MaleA, correspondingly. In other study, Soares et al.[27] have also verified the great ability of several DES to enhance the solubility of kraft lignin. In their work, a different type of DES that maximized lignin solubility was found, namely, urea:propionic acid (U:PA), which allowed 359-fold higher kraft lignin solubility than water.

Thus far, the disclosed data suggest that functional groups in the HBD constituent substantially affect the ability of DES for kraft lignin dissolution, demonstrating the importance of selecting a suitable combination of HBA:HBD for such purpose.

Effect of Water Content on Kraft Lignin Dissolution. The influence of water concentration (5 to 100 wt % content) on the ability of DES to dissolve lignin was also addressed. The solubility of kraft lignin in both alcohol-based DES aqueous solutions and carboxylic acid-based DES aqueous solutions at 313.15 K are shown in Figures 2 and 3, respectively.
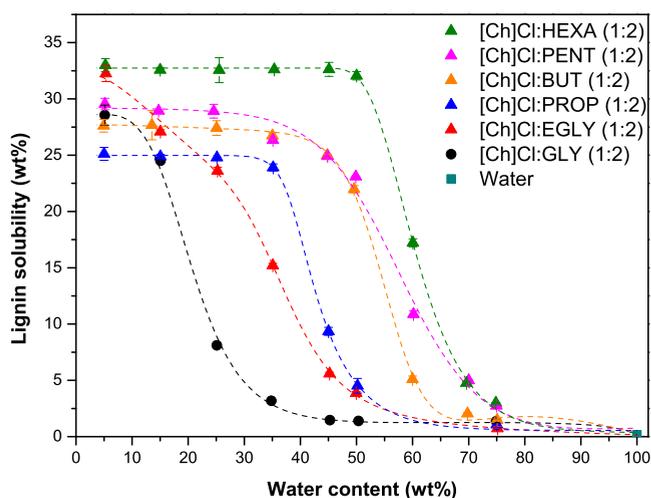

Figure 2. Influence of water content on the solubility of kraft lignin in alcohol-based DES at 323.15 K. All examined DES were tested with the HBA:HBD molar ratio of 1:2. Dashed lines are visual guides.
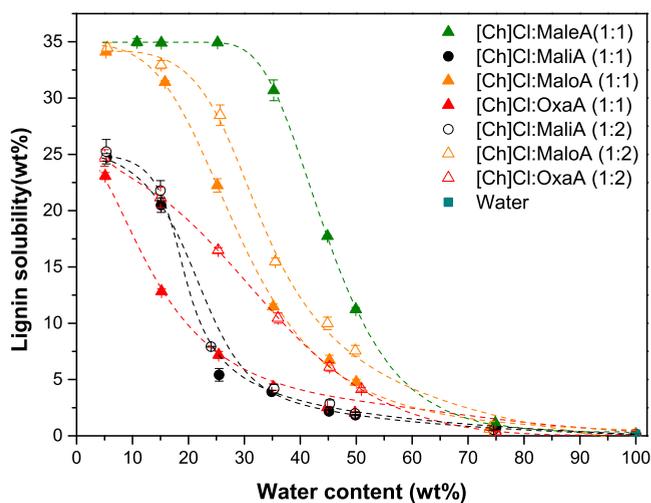

Figure 3. Influence of water content on the solubility of kraft lignin in carboxylic acid-based DES at 323.15 K. All examined DES were tested with the HBA:HBD molar ratio of 1:1 and 1:2. Exceptionally, since a clear liquid is not formed with [Ch]Cl:MaleA (1:2), no lignin solubility data was obtained for this system. Dashed lines are visual guides.

The obtained data with alcohol-based DES systems demonstrated high dependency on water content. The addition of water negatively affected the ability of those DES to dissolve lignin, and depending on the alcohols' chemical structure, different solubility behaviors were observed.[35] For

instance, at 5 wt % water content, [Ch]Cl:EGLY was the second best DES for lignin dissolution among studied solvents, but the addition of 25 wt % water turns this DES the second worst. The negative impact of water was more pronounced for [Ch]Cl:GLY, which enabled only 8.11 wt % lignin solubility at 25 wt % water content. This represents a decrease of more than 70% on the ability of [Ch]Cl:GLY (at 5 wt % water content) to dissolve kraft lignin. The additional hydroxyl group in the GLY's chemical structure in comparison to other HBDs might explain this drastic reduction of lignin solubility in the presence of water. In alcohol-based DES, the hydroxyl groups in the HBD's structure govern hydrogen bond interactions with kraft lignin functional groups, enabling its dissolution in DES. However, water molecules will compete for those interactions hindering the capacity of those DES to promote hydrogen-bonding network with lignin.[36−38] Since GLY comprises three hydroxyl groups in its structure, the impact of water is larger than for other HBDs with only two hydroxyl groups, such as EGlY.[29]

On the other hand, the negative impact of water was less pronounced for [Ch]Cl:PROP, [Ch]Cl:BUT, [Ch]Cl:PENT, and [Ch]Cl:HEXA. In fact, at low water contents, the influence of water is low or negligible on the performance of those DES allowing a plateau on lignin solubility values (Figure 2). For example, [Ch]Cl:PROP presented a stable lignin solubility up to 35 wt % water content. The increase of HBD's carbon chain length enabled higher stability in lignin solubility for higher water contents as observed in the case of [Ch]Cl:HEXA, which maintained lignin solubility near 33 wt % up to approximately 55 wt % water content. Similar observations were reported by Soares et al.[27,28] and Cláudio et al.[39] when using DES and ionic liquids capable of enhancing the solubility of phenolic compounds in aqueous media.

From the obtained lignin solubility curves, it can be inferred that dispersive interactions promoted by HBD's alkyl chains seem to be important to dissolve lignin and to maintain its solubility in aqueous media. However, how do these dispersive forces influence the lignin dissolution process? The sigmoidal shape of the solubility curves using [Ch]Cl:PROP, [Ch]-Cl:BUT, [Ch]Cl:PENT, and [Ch]Cl:HEXA aqueous solutions suggests that the solubility of kraft lignin in these systems is driven by a hydrotropic mechanism.[40,41] These DES, and specially the HBD, self-organize around lignin macromolecules in the presence of water maintaining its solubility. This self-organization is improved with the higher length of HBD's carbon chain as a consequence of stronger dispersive forces between the alkyl chains.

In order to confirm this dissolution mechanism, the kraft lignin solubility curves of these DES aqueous solutions were fitted using the Shimizu and Matubayasi hydrotropy model[41] (Figures S2 and S3 in the Supporting Information). The experimental data could be well described by the model, showing a cooperative hydrotropy as defined by Shimizu and Matubayasi.[41] The sigmoidal profile of the obtained lignin solubility curves suggests a cooperative intermolecular interaction involving hydrotrope molecules participating in the dissolution process as reported by Balasubramanian et al.[42]

A similar effect of water was found in kraft lignin solubility with carboxylic acid-based DES aqueous solutions (Figure 3). For instance, the lignin dissolution performance of [Ch]-Cl:MaleA was not affected by low water contents (up to 25 wt %), which might be related to the alkyl chain length of MaleA (C4). As discussed above, increasing the alkyl chain length of

the HBD may favor lignin dissolution in DES. On the other hand, the presence of an extra hydroxyl group in the C4 alkyl chain length of MaliA had a direct impact on the drastic drop of lignin solubility in [Ch]Cl:MaliA at the same water content range. Besides the steric hindrance discussed above, the existence of an extra hydroxyl group capable of competing for hydrogen bonds with water molecules does not favor lignin dissolution in aqueous media.[43,44] For other studied carboxylic acid-based DES, abrupt decreasing trends in kraft lignin solubility were also observed in the presence of water, which represents cosolvency behavior of those DES.[28]

The data depicted in Figures 2 and 3 also demonstrates that the negative effect of water on kraft lignin solubility is more pronounced in carboxylic acid-based DES than their alcohol counterparts at high water contents. In some cases, the lignin solubility is low or negligible at high water concentrations, showing the antisolvent character of water. Chen et al.[45] reported that the presence of large amounts of water impairs the lignin dissolution capacity of the DES since water molecules compete for hydrogen bonds with the solvent.

Effect of HBA/HBD Molar Ratio on Kraft Lignin Dissolution. The molar ratio between HBA and HBD in DES composition directly impacts its physicochemical properties, including the solvent power for a specific solute. Therefore, the influence of the HBA:HBD molar ratio on kraft lignin solubility was also studied in this work. Three alcohol-based DES ([Ch]Cl:GLY, [Ch]Cl:EGLY, and [Ch]-Cl:HEXA) and four carboxylic acid-based DES ([Ch]Cl:OxaA, [Ch]Cl:MaloA, [Ch]Cl:MaleA, and [Ch]Cl:LacA) with different molar ratios were tested for Kraft lignin solubility at 313.15 K. According to the results presented in Figures 4 and 5, the HBA:HBD molar ratio influenced kraft lignin solubility.

Contrasting the lignin solubility in alcohol-based DES, the highest solubility enhancement was observed for [Ch]-Cl:HEXA (1:2) to around 0.26-fold higher than that for [Ch]Cl:HEXA (1:1) (Figure 4). Similar observation was found when using various HBA:HBD molar ratios studied for [Ch]Cl:GLY and [Ch]Cl:EGLY. Analogously, the increase of
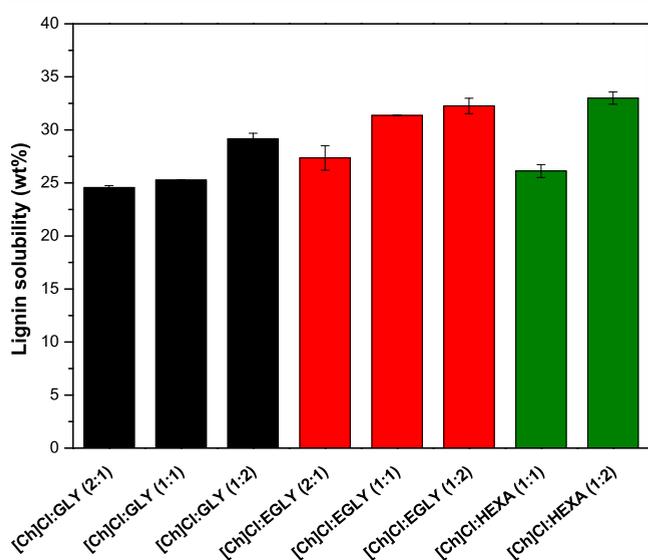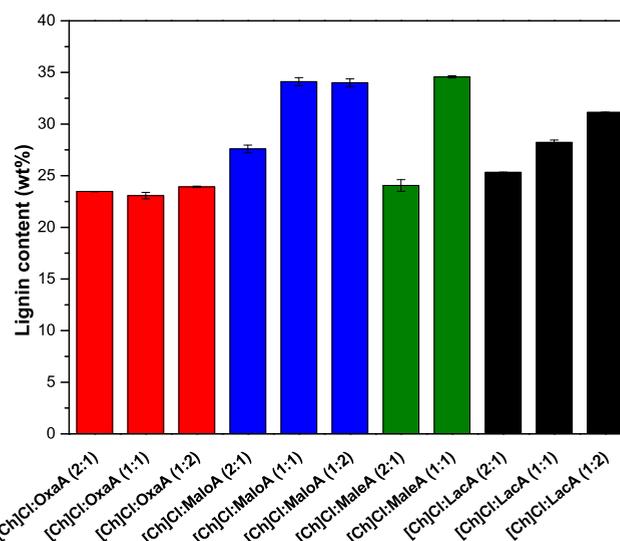

Figure 5. Influence of HBA:HBD molar ratio on the solubility of kraft lignin in carboxylic acid-based DES at 313.15 K. All examined DES were tested at 5 wt % water content. A liquid mixture of [Ch]Cl:MaleA (1:2) was not successfully achieved at 313.15 K.

HBD content in [Ch]Cl:MaleA enabled 40% higher lignin solubility for (2:1) ratio when compared to (1:1) (Figure 5). On the other hand, the lignin solubility enhancement was practically negligible when increasing the OxaA content.

In both cases, alcohol- or carboxylic acid-based DES, a higher HBD molar ratio enhanced lignin solubility. This clearly suggests that HBD exhibits a crucial role in kraft lignin dissolution in DES to the detriment of HBA. Francisco et al.[23] also observed that lignin solubility decreases with increasing amounts of [Ch]Cl (HBA). Moreover, the dispersive interactions favored by long alkyl chain lengths of the HBD (e.g., HEXA and MaleA) favors this solubility improvement rather than short alkyl chain lengths (EGlY and OxaA). This was also highlighted in another study showing the ability of DES to dissolve lignin model compounds.[27]

Structural Changes of Kraft Lignin after Thermal Treatment with DES. The second part of this work addressed the potential of DES to valorize kraft lignin. Kraft lignin was submitted to thermal treatment assisted by DES at 393.15 K for 6 h and was followed by a comprehensive characterization of the regenerated lignin (precipitated with water), including spectroscopic, thermal, and elemental analyses. These conditions were chosen to simulate lignin depolymerization processes usually applied in the literature.[46−48] Four of the above studied DES, namely, [Ch]-Cl:HEXA (1:2), [Ch]Cl:MaleA (1:1), [Ch]Cl:OxaA (1:1), and [Ch]Cl:LacA (1:1), were used for these experimental trials. [Ch]Cl:HEXA (1:2) and [Ch]Cl:MaleA (1:1) were selected because of their highest solubility performances for kraft lignin, while the interest in studying [Ch]Cl:OxaA (1:1) relied on its high acidity. [Ch]Cl:LacA, which has been largely used in biomass delignification processes reported in the literature,[17,49,50] was chosen as the reference.

FTIR−ATR Analysis. The impact of selected DES on the kraft lignin structure was first evaluated by FTIR analysis. The band assignments were performed according to lignin infrared characterization reported in the literature.[51−55] The list of lignin vibrational bands/regions and corresponding assignments are presented in detail in the Supporting Information

Figure 4. Influence of HBA:HBD molar ratio on the solubility of kraft lignin in alcohol-based DES at 313.15 K. All examined DES were tested at 5 wt % water content. A liquid mixture of [Ch]Cl:HEXA (2:1) was not successfully achieved at 313.15 K.

(Table S3) along with full spectra (Figure S4). For comparison, the spectra were organized from kraft lignin at the top to the most modified lignin spectrum at the bottom (Figure 6).
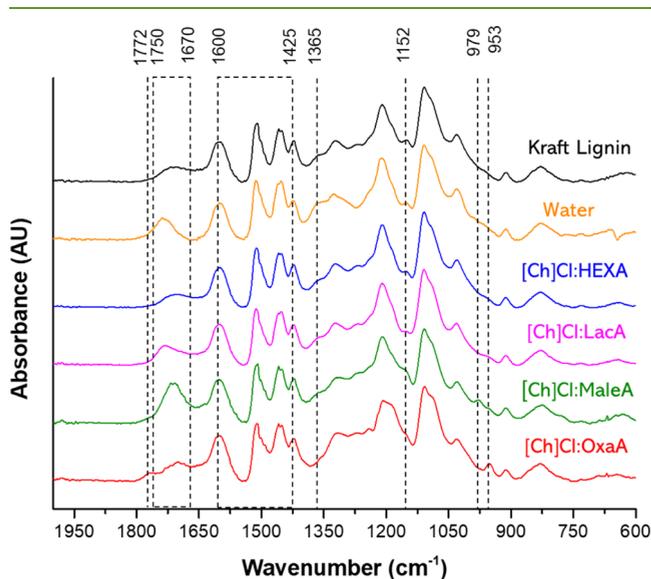

Figure 6. Magnified FTIR−ATR spectra of kraft lignin and recovered lignins from thermal treatments (393.15 K for 6 h) with water, [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1), and [Ch]Cl:OxaA (1:1). All examined DES were tested at 5 wt % water content.

At first sight, all infrared spectra show a typical kraft lignin fingerprint as observed in the region 1750−750 cm^{-1} disclosed in Figure 6. Characteristic kraft lignin absorption bands with notable high intensities at 838, 1109, 1212, 1327, 1456, 1514, and 1600 cm^{-1} were observed in all spectra, suggesting limited changes in the kraft lignin chemical structure after thermal treatments. The lignin recovered from water treatment presented a spectrum similar to that of kraft lignin, showing the ineffective action of water to change lignin structure at studied conditions. Among examined DES, [Ch]Cl:HEXA exhibited nonderivatizing behavior for kraft lignin since the same characteristic vibrational bands were observed for its recovered lignin, and no additional band was detected.

On the other hand, carboxylic acid-based DES demonstrated evidences of lignin chemical modification. For example, [Ch]Cl:LacA−lignin spectrum presented a band shift from 1700 to 1736 cm^{-1} and a simultaneous intensity decrease of the band at 1152 cm^{-1}. The presence of the band at 1736 cm^{-1}

could be associated with C═O stretching in ester groups formed by esterification of lactic acid molecules with lignin hydroxyl groups. This side reaction has also been shown in thermal treatments of lignin model compounds with [Ch]-Cl:LacA.[20] The decreasing intensity of the band at 1152 cm^{-1}, which is assigned to C−O−C vibration in polysaccharides, indicates the removal of residual contents of hemicelluloses and cellulose as a consequence of their acid hydrolysis mediated by the carboxylic acid. Similar trends can also be observed in the FTIR spectra of recovered lignins from the more acidic [Ch]Cl:OxaA and [Ch]Cl:MaleA treatments. Moreover, additional bands at 953 and 979 cm^{-1} were observed in [Ch]Cl:OxaA−lignin and [Ch]Cl:MaleA−lignin spectra, respectively, suggesting possible variations of lignin chemical structure or contamination of [Ch]Cl:OxaA and [Ch]Cl:MaleA.

Elemental Analysis. The results obtained from the elemental analysis (Table 2) of recovered lignins showed a minimal impact of the thermal treatments on carbon, hydrogen, and oxygen contents, although at much less content, a sharp variation of nitrogen in lignins recovered from thermal treatments with carboxylic-based DES was observed. This is mostly pronounced in [Ch]Cl:MaleA−lignin and [Ch]-Cl:OxaA−lignin samples, in which the nitrogen content increased almost 2.6- and 4.7-fold the original content in kraft lignin. These results indicate a contamination of [Ch]Cl in those lignin samples, supporting the conclusions inferred from the FTIR data. On the other hand, the sulfur content in lignin samples followed an opposite trend. The 2 wt % sulfur content in kraft lignin was substantially reduced with thermal treatments, especially with carboxylic-acid DES. For instance, the treatments with [Ch]Cl:MaleA and [Ch]Cl:OxaA allowed a sulfur content reduction to almost half of the original. It should be emphasized that sulfur content is one the major deterrents of kraft lignin valorization, and thus its removal is beneficial.[56,57]

2D HQSC NMR Analysis. The structural analysis of lignin samples was complemented with the 2D HQSC NMR technique to better understand the impact of thermal treatments with DES. The HSQC oxygenated and aromatic regions of the kraft lignin along with the representation of identified lignin subunits are shown in the Supporting Information (Figure S5) to suitably address its chemical characterization. The ^{13}C−^{1}H cross signal assignments are also described in the Supporting Information (Table S4) according to data reported in the literature.[3,4,58−62]

The HSQC analysis of recovered lignin samples from thermal treatments with [Ch]Cl:HEXA, [Ch]Cl:LacA, [Ch]-Cl:MaleA, and [Ch]Cl:OxaA revealed different behaviors

Table 2. Elemental Characterization of Kraft Lignin and Recovered Lignins from Thermal Treatments (393.15 K for 6 h) with Water, [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1), and [Ch]Cl:OxaA (1:1)[a]

samples	elemental analysis (wt %)				
	C	H	N	S	O
kraft lignin	60.71 ± 0.29	5.35 ± 0.03	0.14 ± 0.01	2.00 ± 0.15	30.37 ± 0.28
water−lignin	63.03 ± 0.13	5.55 ± 0.02	0.13 ± 0.00	1.47 ± 0.01	28.22 ± 0.26
[Ch]Cl:HEXA−lignin	63.38 ± 0.00	5.66 ± 0.07	0.15 ± 0.01	1.46 ± 0.26	28.47 ± 0.40
[Ch]Cl:LacA−lignin	63.58 ± 0.09	5.34 ± 0.09	0.24 ± 0.00	1.33 ± 0.03	27.82 ± 0.13
[Ch]Cl:MaleA−lignin	61.89 ± 0.20	5.26 ± 0.04	0.36 ± 0.00	1.17 ± 0.21	30.00 ± 0.23
[Ch]Cl:OxaA−lignin	62.59 ± 0.35	5.39 ± 0.04	0.66 ± 0.01	1.15 ± 0.36	29.32 ± 0.80

[a]All examined DES were tested at 5 wt % water content. The data is expressed as means and corresponding standard deviations.
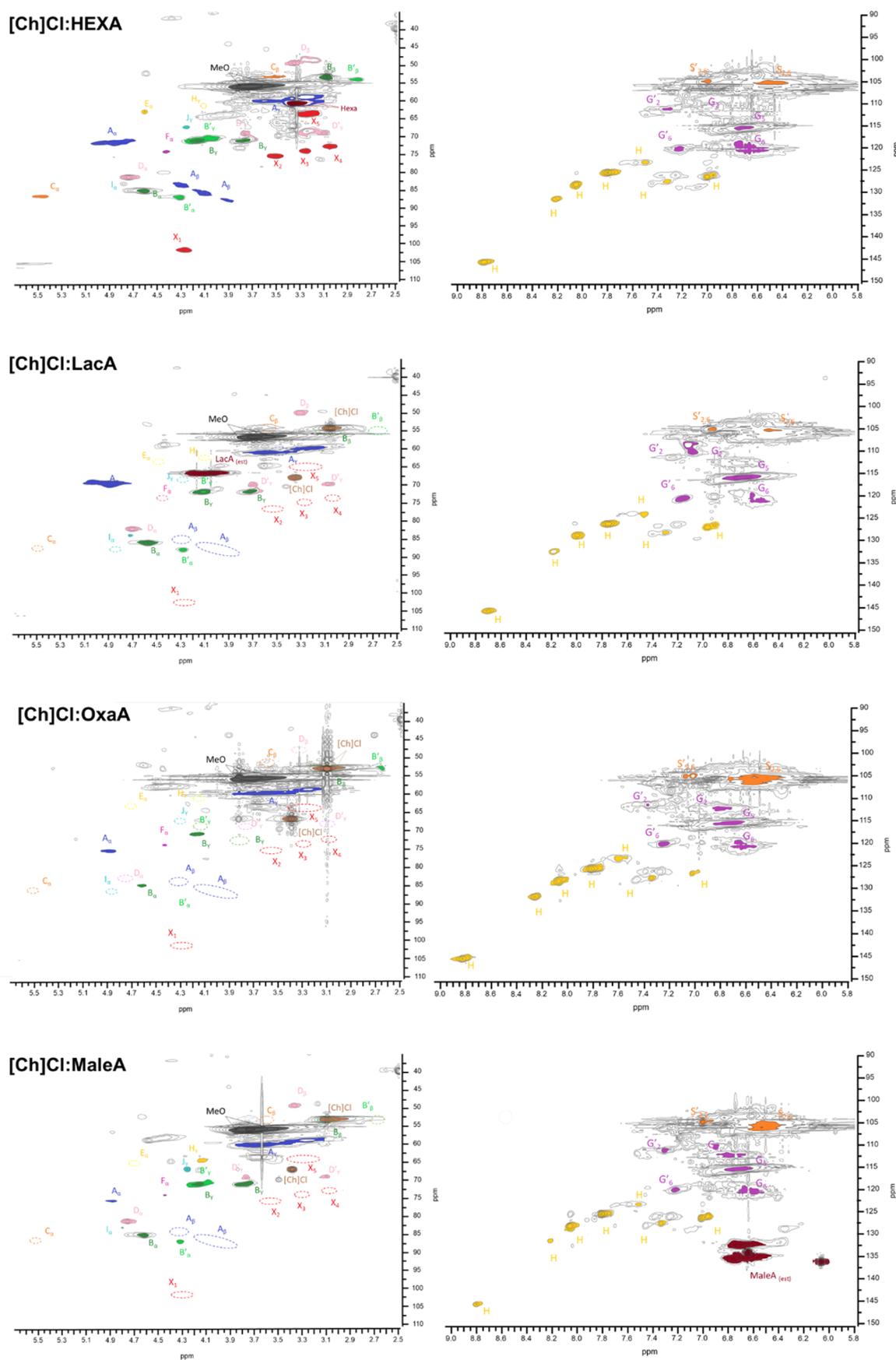
Figure 7. 2D HSQC NMR of recovered lignins from thermal treatments (393.15 K for 6 h) with [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1), and [Ch]Cl:OxaA (1:1). All examined DES were tested at 5 wt % water content. The corresponding $^{13}C-^1H$ cross signals of main lignin substructures are assigned, while resonances related to DES contamination were also attributed.
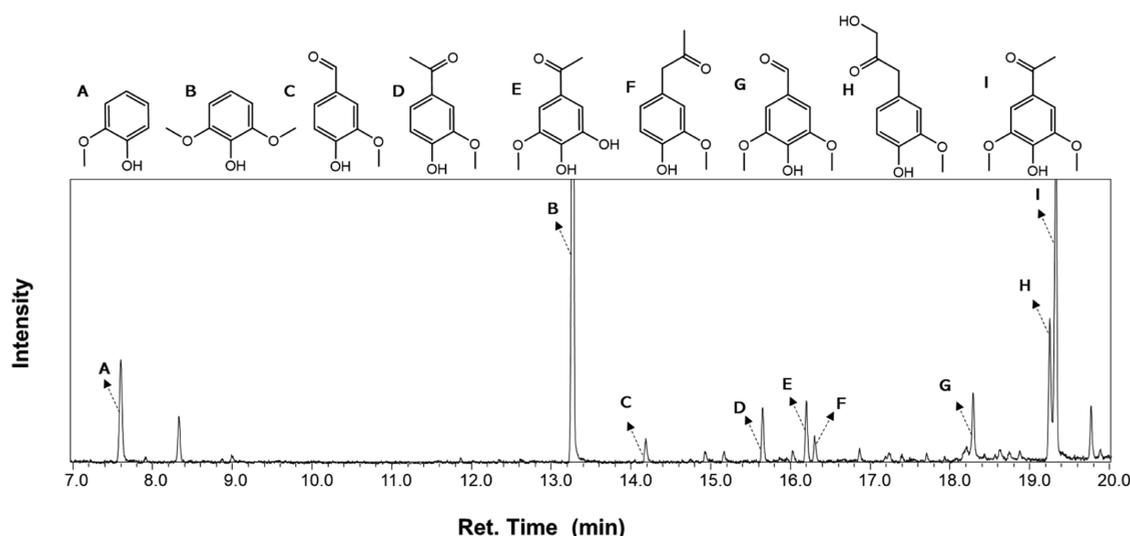
H

Figure 8. GC chromatogram of the liquid phase from kraft lignin treatment with [Ch]Cl:OxaA (393.15 K—6 h) showing the following aromatic compounds: (A) Guaiacol, (B) syringol, (C) vanillin, (D) acetovanillone, (E) 3,4-dihydroxy-5-methoxyacetophenone, (F) guaiacylacetone, (G) syringaldehyde, (H) 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone, and (I) acetosyringone.

between these DES regarding their capacity to modify the lignin structure. The HSQC spectra of recovered lignins after thermal treatment with these DES are depicted in Figure 7.

Notably, the HSQC spectra of both kraft lignin (Figure S5) and [Ch]Cl:HEXA−lignin (Figure 7) share the same identified C−H correlations and intensities, which means that no relevant chemical modification to the kraft lignin structure was governed by [Ch]Cl:HEXA. The same behavior was observed for kraft lignin treated with water (Figure S6). Therefore, lignin chemical linkages are not altered using [Ch]Cl:HEXA or water at the examined temperature (393.15 K).

On the other hand, carboxylic-based DES enabled the disruption of important lignin chemical bonds, specially C−O covalent bonds, whereas different levels of structural modification were observed. The HSQC spectra of recovered lignins demonstrated an increased reactivity of examined DES in the following order: [Ch]Cl:LacA < [Ch]Cl:MaleA < [Ch]Cl:OxaA. In all cases, an absence of C_β−H_β correlation of the alkyl−aryl ether structures (A) at 83.96/4.31 ppm (guaiacyl type) and 87.23/3.69 ppm (syringyl type) was observed. On the other hand, the cross signals from α (81.36/4.78 ppm) and γ (59.0/3.2 and 59.9/3.7 ppm) positions in the same substructure were maintained, although depicting different intensities among spectra. These results suggest that the acidity provided by these carboxylic-based DES allowed the cleavage of β-O-4 bonds in lignin macromolecules. Furthermore, all signals related to phenylcoumaran substructures (C) vanished, representing the cleavage of α-O-4 chemical linkages in lignin. On the other hand, other relevant lignin substructures, including pinoresinol (B) and spirodienone (D), were maintained in kraft lignin treated with [Ch]Cl:LacA and [Ch]Cl:MaleA. This was not observed for [Ch]Cl:OxaA− lignin spectrum, in which the cross signals from the spirodienone substructure (D) were not visible. It possibly indicates the higher capacity of oxalic acid for the cleavage of α-O-α linkages, which could be associated with its higher acidity (pka1$_{(OxaA)}$ = 1.42) than their acid counterparts (pka1$_{(MaleA)}$ = 1.94; pka1$_{(LacA)}$ = 3.86). Unsurprisingly, the cross signals related to xylan backbone, namely, at 63.63/3.28

ppm (X_5), 72.85/3.06 ppm (X_4), 74.28/3.28 ppm (X_3), 75.84/ 3.53 ppm (X_2), and 101.80/4.29 ppm (X_1), disappeared in all cases, indicating the removal of residual xylan present in kraft lignin through acid hydrolysis of the carbohydrate glycosidic linkage mediated by carboxylic acid-based DES.

To confirm the high reactivity of [Ch]Cl:OxaA, a standard gas chromatography/mass spectrometry (GC/MS) analysis of the liquid phase obtained after kraft lignin thermal treatment with this DES was performed. The acquired GC chromato-gram (Figure 8) depicted the existence of several lignin monomers, either S or G type unit, in the liquid phase after the thermal treatment. A total of nine meaningful aromatic compounds were identified by contrasting with standard compounds and GC/MS databases. It is reasonable to mention that these compounds were formed by lignin depolymerization, mostly through C−O cleavage assisted by [Ch]Cl:OxaA as mentioned above, but the obtained depolymerization profile also reveals possible C−C cleavage. For instance, guaiacol (A) and syringol (B) were detected and were probably formed from the cleavage of the aliphatic part of lignin phenyl-propanoid units and/or other identified compounds (C to I in Figure 8). Yet, more data is needed to elucidate this result. Overall, these results indicate that [Ch]Cl:OxaA can act as both the solvent and the catalytic agent, resulting in partial lignin depolymerization and subsequent structural modifica-tion as shown by the HSCQ analysis.

The HSQC data also revealed the presence of DES as a contaminant in all treated lignins. Resonances associated with [Ch] ion, such as CH_3 (54.50/3.30 ppm) and CH_2 (67.0/3.41 ppm) groups, were identified in the spectra of recovered lignins from treatments with carboxylic-based DES. This result is corroborated by the substantial increase in the amount of nitrogen in those lignins found by elemental analysis as presented above (Table 2). The fact that [Ch] is not present in the [Ch]Cl:HEXA−lignin spectrum suggests that a chemical binding between [Ch] and lignin might be favored in acidic media. Alvarez-Vasco et al. also proposed a possible reaction between [Ch] and lignin phenolic groups (lactic acid was used as HBD).[17] Furthermore, cross signals attributed to carboxylic acids, such as lactic and maleic acids, were also found in HSQC
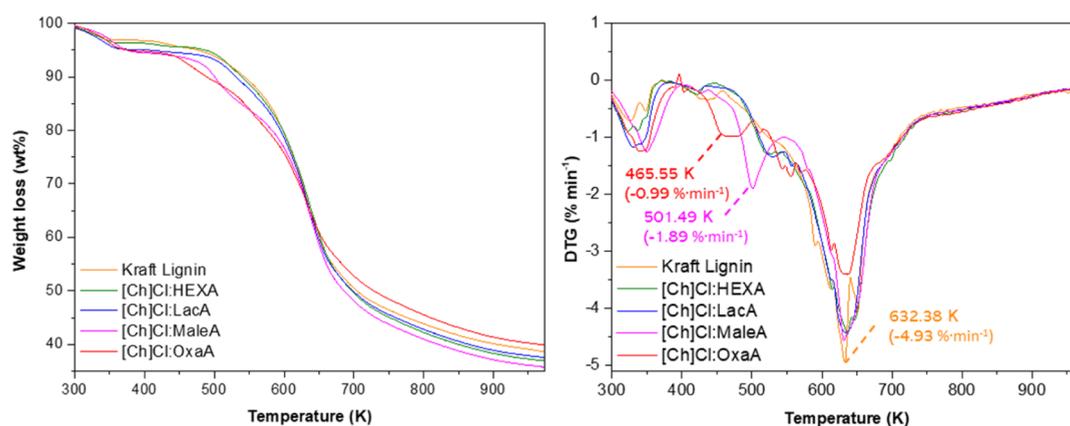
Figure 9. TGA (left) and DTGA (right) curves of kraft lignin and recovered lignins from thermal treatments (393.15 K for 6 h) with [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1), and [Ch]Cl:OxaA (1:1). All examined DES were tested at 5 wt % water content.

spectra. Obviously, carboxylic signals from oxalic acid are not seen in HSQC (lack of C−H coupling), but its presence was confirmed by 1D NMR (data not shown). The esterification of these carboxylic acids with lignin hydroxyl groups is most likely to occur as indicated by the intense C═O vibrational bands in FTIR spectra previously reported (Figure 6).

A comparison between aromatic regions of HSQC spectra clearly shows that the aromatic fractions of kraft lignin are practically preserved, including S and G type units as well as *p*-hydroxycinnamyl structures (H), after DES treatment. Although [Ch]Cl:OxaA demonstrated the ability for lignin depolymerization, the formation of depolymerized products from S and G type units (Figure 8) indicates no selective cleavage.

FTIR, elemental analysis, and 2D NMR data elucidated the chemical modifications of kraft lignin in the presence of alcohol- and acid-based DES. On the one hand, the nonderivatizing behavior of alcohol-based DES, such as [Ch]Cl:HEXA, allows their application as solvents for the design of tailored reactions of lignin into new products. On the other hand, carboxylic acid-based DES showed the ability to depolymerize lignin in valuable monomeric compounds through ether bond cleavage increasing the value of kraft lignin, but part of the solvent seems to react with the remaining non-depolymerized fraction by esterification. Although consumption of the solvent would be seen as a negative effect, in this case, the integration of dissolution and functionalization of lignin with esterified carboxylic acids may be envisaged as an opportunity to increase the cost efficiency in the production of new lignin bio-based composites and materials. For instance, lignin esters of maleic acid have been used for the improvement of lignin reactivity toward grafting reactions in thermal processes[63] as well as for the functionalization of lignin nanoparticles as plastic fillers.[64]

TGA Analysis. The thermal stability of kraft lignin and DES-treated lignins was also addressed. Figure 9 shows the thermal decomposition curves and corresponding derivatives in the temperature range between 303.15 and 973.15 K.

The TGA data demonstrated that treated lignins exhibited thermal profiles similar to that of kraft lignin. Yet, relevant differences can be highlighted. Among examined samples, [Ch]Cl:MaleA−lignin and [Ch]Cl:OxaA−lignin showed the highest mass loss between 350 and 600 K. However, after this temperature range, [Ch]Cl:OxaA−lignin demonstrated higher thermal stability (60.1 wt % loss) than others (62.5−64.2 wt %

loss), including kraft lignin (61.4 wt % loss) as depicted in Figure 9. The higher thermal stability of [Ch]Cl:OxaA−lignin can be correlated with its composition of recalcitrant structures, such as pinoresinol containing $\beta-\beta$ linkages, to the detriment of more susceptible structures for cleavage (*e.g.*, aryl ether) as depicted in HSQC spectra. Furthermore, the high reactivity of [Ch]Cl:OxaA not only favors the cleavage of aryl ether structures but also may enable the formation of lignin condensed fractions difficult to pyrolyze. After ether bond cleavage, radical couplings could be formed, which in turn establish intricate inter/intra C−O and inter C−C bonds that require high dissociation energies.[65]

On the other hand, the highest mass loss of lignins treated with [Ch]Cl:OxaA−lignin and [Ch]Cl:MaleA at 350−600 K range mentioned above is clearly expressed in differential thermogravimetric analysis (DTGA) curves with peaks of weight loss rate at 465.55 and 501.49 K, respectively (Figure 9). In contrast to literature data, these mass losses are most likely to be representative of oxalic and malic acid contaminations.[66,67] This reflects the identified contaminations observed before in NMR analysis. Moreover, the maximum differential thermogravimetric values (DTG$_{max}$) were detected between 625 and 640 K for all lignin samples. This mass loss is related to the fragmentation of lignin interunit bonds[68] and seems to be quite similar between almost all lignin samples with no grid differences when compared to kraft lignin. An exception can be observed for [Ch]Cl:OxaA−lignin (Figure 9), which follows a different pattern represented by a lower weight loss rate and a slight DTG$_{max}$ deviation. This can be associated with lignin chemical changes induced by [Ch]Cl:OxaA as explained before.

■ CONCLUSIONS

The present work demonstrated the ability of DES to dissolve kraft lignin and their potential to chemically modify this underrated byproduct of pulp and paper industries.

The obtained results showed that DES HBD plays an important role in kraft lignin dissolution, and the efficiency is governed by its chemical nature (alcohol or carboxylic), chain length, and molar ratio to HBA. Furthermore, the addition of water negatively affects the lignin solvation power of DES. Among the examined DES, [Ch]Cl:HEXA and [Ch]Cl:MaleA showed the best performance for kraft lignin dissolution, allowing 32.99 and 34.97 wt % solubility at 313.15 K, respectively.

Besides, the thermal treatments (393 K) of kraft lignin with selected DES demonstrated that carboxylic acid-based DES induce chemical modifications to kraft lignin, especially, the disruption of C−O covalent bonds (e.g., β-O-4, α-O-4, and α-O-α). Furthermore, the acidity power of carboxylic acid-based DES has a direct impact on the chemical modification of kraft lignin, while alcohol-based DES were found to be excellent nonderivatizing solvents by maintaining the lignin chemical structure.

The results shown in this work highlight the versatility of these solvents, which, depending on their chemical structure and composition, may offer different lignin valorization pathways: (i) partial lignin depolymerization with carboxylic acid-based DES into added value low-molecular-weight compounds and simultaneous esterification of the non-depolymerized fraction as a precursor to new product formulations or (ii) dissolution of underivatized lignin for target modifications using alcohol-based DES toward new bio-based materials.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c06655.

List of compounds used in this work; kraft lignin calibration curve; kraft lignin solubility data; description of Shimizu and Matubayasi hydrotropy model and correlation with solubility data; lignin characterization; and spectra and assignments of FTIR−ATR and 2D HSQC (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

André M. da Costa Lopes − CICECO☐Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal; CECOLAB☐Collaborative Laboratory towards Circular Economy, Oliveira do Hospital 3405-155, Portugal; ⓞ orcid.org/0000-0001-8855-6406; Email: andremcl@ua.pt

João A. P. Coutinho − CICECO☐Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal; ⓞ orcid.org/0000-0002-3841-743X; Email: jcoutinho@ua.pt

Authors

Filipe H. B. Sosa − School of Chemical Engineering (FEQ), University of Campinas (UNICAMP), Campinas 13083-852, São Paulo, Brazil; CICECO☐Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal

Dinis O. Abranches − CICECO☐Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal; ⓞ orcid.org/0000-0003-0097-2072

Mariana C. da Costa − School of Chemical Engineering (FEQ), University of Campinas (UNICAMP), Campinas 13083-852, São Paulo, Brazil

Complete contact information is available at:
https://pubs.acs.org/10.1021/acssuschemeng.0c06655

Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

DES, deep eutectic solvent; HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; [Ch]Cl, cholinium chloride; EGLY, ethylene glycol; GLY, glycerol; PROP, 1,3-propanediol; BUT, 1,4-butanediol; PENT, 1,5-pentanediol; HEXA, 1,6-hexanediol; OxaA, oxalic acid; MaloA, malonic acid; MaleA, maleic acid; MaliA, malic acid; LacA, lactic acid

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