

Kraft lignin solubility and its chemical modification in deep eutectic solvents

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

17

18 **KEYWORDS.** Deep eutectic solvents; Kraft lignin; Solubility; Hydrotrophy; Depolymerization; Non-
19 derivatization.

20 INTRODUCTION

21 Lignin is considered the second most abundant natural macromolecule on the planet (after
22 cellulose) and represents an important source of aromatic compounds.¹ The lignin chemical
23 structure is characterized by randomly linked interunit bonds, such as ether (*e.g.* β -O-4, α -O-4,
24 4-O-5) and carbon-carbon (*e.g.* 5-5', β -5, β -1, β - β) linkages, established between three
25 phenylpropanoid units: *p*-coumaryl, coniferyl, and sinapyl alcohols. This allows lignin to present
26 an amorphous and rather complex structure, acting as a glue to give hardness to plant biomass
27 and to protect from microbial attacks.¹

28 One of the most abundant sources of lignin comes from the activity of pulp and paper
29 companies. The production of cellulose pulp from wood is generally performed by delignification
30 processes, being the Kraft process one of the most applied in industry, producing Kraft lignin as
31 by-product. Traditionally, Kraft lignin is used as feedstock in boilers, where it is burnt to generate
32 energy to the factory grid.² However, pulp and paper companies has shown an increasing
33 interest for the valorization of this by-product as precursor to produce added value chemicals
34 and materials³ rather than its combustion. However, Kraft lignin is poorly soluble in water, while
35 a lack of cheap, efficient and environmentally safe solvents for lignin dissolution is preventing
36 its successful valorization . In this context, a promising green and eco-friendly approach for lignin
37 dissolution relies on the deployment of a class of solvents known as deep eutectic solvents (DES).
38 DES, first introduced by Abbott et al.,⁴ are mixtures of two or more components capable of
39 establishing hydrogen bond interactions and enabling a significant negative deviation of the
40 mixture's melting temperature from that predicted for an ideal mixture.⁵ This depression in
41 melting temperature makes some of the existing DES to be liquid at room temperature and
42 further used as solvents in a plethora of applications. Generally, two components are used in
43 their preparation, including a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD).
44 Quaternary ammonium salts, mostly cholinium chloride ([Ch]Cl), stand as most used HBA
45 components, due to their low cost, low toxicity, biodegradability and easy preparation.⁶

46 Substances such as urea, alcohols,⁷ fatty alcohols or fatty acids,⁸ sugar and carboxylic acids⁹ have
47 been often applied as HBD. Therefore, DES can be considered as alternative to conventional
48 organic solvents, which (part of them) are generally volatile, flammable, explosive and toxic.¹⁰
49 There has been an increasing number of studies showing the successful application of DES as
50 powerful solvents for biomass delignification.¹¹⁻¹³ However, the study of lignin dissolution in
51 DES, especially technical lignins from well-established delignification processes (*e.g.* Kraft
52 pulping), towards their further valorization is still barely examined.^{14,15} Francisco et al.¹⁶
53 investigated a wide range of DES to dissolve low sulfonated Kraft lignin and cellulose. The
54 authors used carboxylic acids as HBD, while alanine, betaine, [Ch]Cl, glycine, histidine, proline,
55 and nicotinic acid were chosen as HBA. Most of the examined DES showed high lignin solubility,
56 but little or negligible solubility of cellulose, demonstrating the high selectivity of these solvents
57 for lignin dissolution. Among tested DES, betaine:malic acid (1:3) exhibited the best performance
58 for lignin dissolution. In other work, Lynam *et al.*¹⁷ studied the dissolution of Kraft lignin in
59 several DES, which demonstrated capacity to dissolve between 9 % and 14 % ($w_{\text{lignin}}/w_{\text{DES}}$) at
60 333.15 K. [Ch]Cl:formic acid (1:2) was found the best HBA:HBD combination for Kraft lignin
61 dissolution.¹⁷

62 The use of DES aqueous systems has also arisen the interest to solubilize technical lignins. Xue-
63 Dan Hou et al.¹⁸ observed that small amounts of water (5 wt%) negatively affected lignin
64 solubility in [Ch]Cl:urea (1:2), while an opposite trend was highlighted for proline:malic acid (3:1)
65 and [Ch]Cl:oxalic acid (2:1) at same water content. For instance, adding 5 wt% water content to
66 proline:malic acid (3:1) increased the solubility of Kraft lignin from 2.7 wt% to 9.4 wt%. The
67 differences observed in the effect of water on lignin solubility by those DES were suggested to
68 be dependent of DES chemical nature (basicity vs acidity). The addition of water was beneficial
69 for acid-based DES rather than non-acidic [Ch]Cl:urea (1:2). In other study, Yiin et al.¹⁹ also
70 observed that lignin solubility in malic acid:sucrose:water systems was improved from 6.38 to
71 9.16 wt% with increasing molar ratio of water from 1:1:1 to 1:1:10.¹⁸ A more detailed study upon

72 lignin dissolution in DES aqueous solutions was performed by Soares et al.^{20,21} Their work
73 showed that some DES act as hydrotropes enabling lignin dissolution in aqueous media.²⁰ For
74 example, urea:propionic acid (1:2) at 50 wt% water content dissolved three times more Kraft
75 lignin than neat DES. The hydrotropic mechanism was confirmed by dynamic light scattering.
76 The same authors investigated the ability of DES to act as hydrotropes or co-solvents in aqueous
77 solutions using lignin model compounds, Kraft and Organosolv lignins.²¹ The hydrotropic
78 mechanism led to urea:propionic acid (1:2) aqueous solution a notable increase in Kraft lignin
79 solubility by about 228-fold the solubility in water, while the co-solvency provided by
80 tetrabutylphosphonium chloride:ethylene glycol allowed an improvement of about 163-fold. In
81 the latter, water revealed to be a negative factor in lignin dissolution.²¹
82 Few studies have engaged efforts to study the fundamentals of the lignin dissolution mechanism
83 in DES, while the chemical modifications in lignin structure during dissolution has been barely
84 tackled. Therefore, the present study aimed at understanding the solubility of Kraft lignin in
85 different DES and their aqueous solutions in the first place at 313.15 K and further evaluating
86 the chemical modifications in Kraft lignin structure at high temperature (393.15 K) to ascertain
87 a successful strategy for the valorization of this technical lignin assisted by DES.

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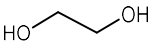
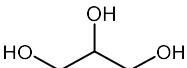
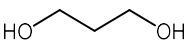
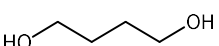
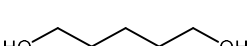
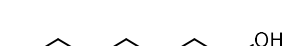
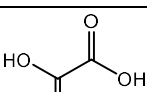
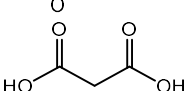
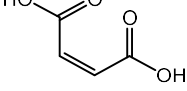
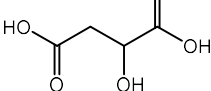
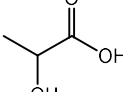
89 **MATERIALS AND METHODS**

90 **Chemicals.** The preparation of DES studied in this work involved combinations of cholinium
91 chloride ([Ch]Cl) with the following compounds: glycerol (GLY), ethylene glycol (EGLY), 1,3-
92 propanediol (PROP), 1,4-butanediol (BUT), 1,5-pentanediol (PENT), 1,6-hexanediol (HEXA) as
93 well as lactic (LacA), oxalic (OxaA), malic (MaliA), malonic (MaloA) and maleic (MaleA) acids. All
94 chemicals were used as received and their water content was measured using a Metrohm 831
95 Karl Fischer coulometric titrator (Table S1 in SI). Their chemical structures and HBA:HBD molar
96 ratios studied in this work are depicted in Table 1. Kraft Lignin from Eucalyptus Urograndis was
97 directly supplied by Suzano Papel & Celulose (Brazil). It was isolated employing carbon dioxide

98 (CO₂) to the industrial black liquor resulting in a Kraft lignin solid sample composed of 95% lignin,
 99 2 % xylans, and 3 % ash contents with Mw=1520 g mol⁻¹, Mn=1345 g mol⁻¹, and PDI = 1.13.

100

101 **Table 1.** List of DES used in this study.

DES	HBD's chemical structures	Molar Ratio (HBA:HBD)
<i>Alcohols</i>		
[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
<i>Carboxylic acids</i>		
[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

102 ^aused in this study as reference

103

104 **DES preparation.** Specific molar amounts of [Ch]Cl and corresponding HBD (see Table 1) were
 105 placed in sealed glass vials with a stir bar and heated in a paraffin bath at 333.15 ± 0.01 K with
 106 constant stirring until a clear liquid was achieved.⁹ The water content in prepared DES was

107 measured using a Metrohm 831 Karl Fischer coulometer and the obtained values were
108 considered for the preparation of DES aqueous solutions (5, 15, 25, 35, 45, 50, 75 wt% water
109 content). These aqueous solutions were prepared by diluting the neat DES in distilled water.

110

111 **Lignin solubility assays.** An excess of Kraft lignin was added to 2.00 ± 0.01 g of DES (or its
112 aqueous solution) in glass flasks with a magnetic stirring bar. The vials were sealed and placed
113 in an aluminum block holder that was transferred to a heating plate temperature control (PT100)
114 magnetic stirrer (Series H03D from LBX Instruments). Solubility tests were performed at 313.15
115 K under constant stirring at 150-200 rpm. The samples were kept under agitation until reaching
116 saturation state and then were filtered using PTFE filters (0.45 μm pore size) to remove
117 undissolved solid lignin. The saturated liquid phase was diluted with dimethyl sulfoxide (99.98
118 %, Fischer Scientific, EUA) and lignin concentration was quantified at a wavelength of 280 nm by
119 UV spectroscopy (Synergy HTX Multi-Mode Reader from BioTek Instruments). Lignin calibration
120 curves using known amounts of the same Kraft lignin sample dissolved in DMSO were performed
121 (at 280 nm wavelength) for the determination of lignin solubility (Figure S1 shows an example).
122 All solubility tests were performed in duplicates. The Kraft lignin solubility was calculated by the
123 following equation:

$$124 \quad \text{lignin wt\%} = \frac{m_{\text{lignin}}(g)}{m_{\text{DES}}(g)} \times 100$$

125

126 **Thermal treatment of Kraft lignin.** A sample of Kraft lignin (600 mg) was added to 3.00 ± 0.01
127 grams of DES (5 wt% water content) in a glass tube reactor with a stirring bar. The tubes were
128 sealed and placed in a Radleys Carousel Tech (Radleys, United Kingdom) for 6 hours at 393.15 K
129 and kept under agitation. After treatment, 15 mL of cold distilled water (283.15 K) were added
130 to the resulting solution and mixed in a vortex stirrer (VWR international Reax Top) to promote
131 lignin precipitation. The solution was then introduced into an ice bath to increase the
132 precipitation efficiency. The precipitated lignin was filtered by vacuum and washed with distilled

133 water (200 mL) to ensure DES removal. The obtained solid was oven-dried at 323.15 K to a
134 constant weight and the amount of precipitated lignin was determined gravimetrically. A blank
135 experiment using water was performed at the same conditions.

136

137 **Fourier Transform Infrared with Attenuated Total Reflection Analysis (FTIR-ATR).** The FTIR
138 spectra of lignin samples were recorded on a PerkinElmer Spectrum BX spectrometer equipped
139 with a horizontal Golden Gate ATR cell and a diamond crystal. A total of 32 scans were acquired
140 in absorbance units for each sample with a resolution of 4 cm⁻¹ and wavenumber range between
141 4000 cm⁻¹ and 400 cm⁻¹.

142

143 **Two-dimensional Heteronuclear Single Quantum Correlation Nuclear Magnetic Resonance**
144 **spectroscopy (2D HSQC NMR).** Approximately 60 mg of lignin sample was carefully mixed in 500
145 μL DMSO-*d*₆ with TMS as the internal reference. After complete dissolution, the resulting
146 solution was transferred to an NMR tube. The Two-dimensional ¹H-¹³C chemical shift correlation
147 HSQC NMRs were acquired on Bruker AVANCE 500 MHz NMR spectrometer (Bruker, Billerica,
148 MA) equipped with an inverse gradient 5 mm TXI ¹H/¹³C/¹⁵N cryoprobe, using the Bruker-
149 supplied pulse sequence “hsqcetgp” with 2D H-1/X correlation via double inept transfer (trim
150 pulses), Echo/Antiecho-TPPI gradient selection for phase sensitivity improvement, and
151 decoupling during acquisition. The chemical shifts were calibrated with respect to the DMSO
152 solvents peaks (2.49 ppm for residual proton and 39.5 ppm for ¹³C). All the experiments were
153 carried out at 298.15 K with the following parameters: spectral width of 11 ppm in the F2 (¹H)
154 dimension and 165 ppm in the F1 (¹³C) with 1024 data points, 194 scans and recycle delay of 1.5
155 seconds.

156

157 **Thermal Gravimetric Analysis (TGA).** Thermogravimetric experiments were carried out in a
158 differential thermogravimetric analyzer (TGA-50 Shimadzu). Approximately 5 mg of lignin
159 sample was placed in an aluminum pan and further analyzed under nitrogen gas blanket using

160 a flow rate of 50 ml/min. The samples were heated at a rate of 10 °C min⁻¹ with a temperature
161 range of 30–700 °C.

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

165

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

183

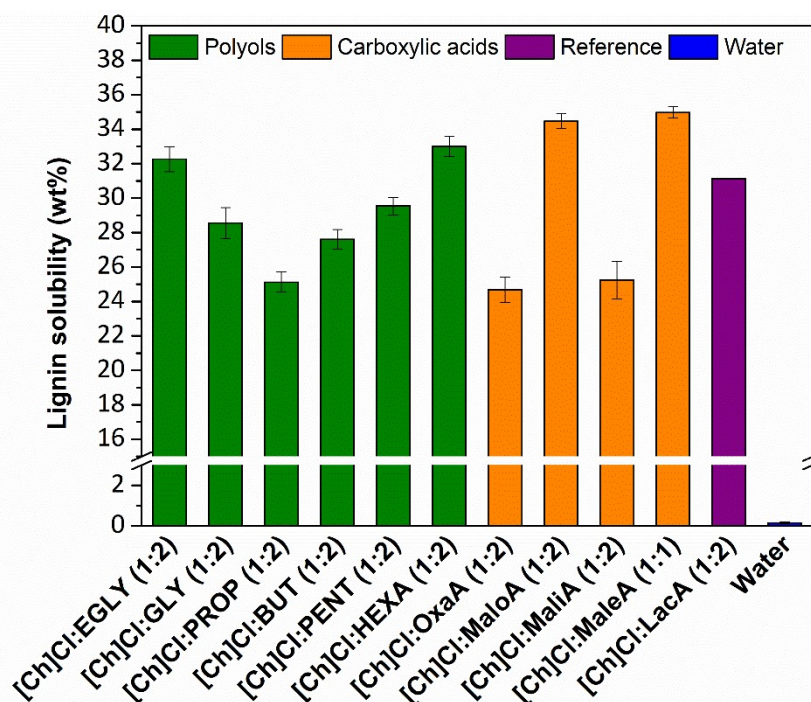
184 **RESULTS AND DISCUSSION**

185 **The effect of the HBD on Kraft lignin dissolution.** The importance of the HBD component in DES
186 to dissolve lignin was first evaluated. DES composed of alcohols and carboxylic acids were

187 examined for Kraft lignin dissolution at 313.15 K and the solubility values are presented in Figure
188 1 (also in Table S2 in SI).

189 According to the obtained results, the ability of alcohol-based DES to dissolve Kraft lignin can be
190 ordered as follows: [Ch]Cl:HEXA > [Ch]Cl:EGLY > [Ch]Cl:PENT > [Ch]Cl:GLY > [Ch]Cl:BUT >
191 [Ch]Cl:PROP. Among the examined alcohol-based DES, [Ch]Cl:HEXA showed the best
192 performance for lignin dissolution, reaching a value of 32.99 ± 0.58 wt% lignin solubility at
193 313.15 K. Furthermore, a crescent trend in lignin solubility with the increase of the carbon chain
194 length of the alcohol was observed. This is pronounced between [Ch]Cl:PROP and [Ch]Cl:HEXA
195 (C3 to C6), but an exception was observed for EGLY-based DES, which presented a higher lignin
196 solubility than PROP, BUT and PENT counterparts. In case of [Ch]Cl:EGLY, the smaller size of the
197 HBD may favor the interaction with lignin, improving its solubility. However, despite the fact
198 that [Ch]Cl:HEXA and [Ch]Cl:EGLY showed similar values of Kraft lignin solubility, the dissolution
199 mechanism may differ between these two DES (this is explored in the next subsection).
200 Furthermore, the presence of an extra hydroxyl group in the alcohol carbon chain allowed an
201 enhancement in lignin solubility ([Ch]Cl:PROP vs [Ch]Cl:GLY). Contrasting both C3 chain length
202 PROP and GLY, the latter's extra hydroxyl group allows an additional site to establish hydrogen
203 bonding interactions with the Kraft lignin functional groups (hydroxyl, carbonyl and carboxylic),
204 enhancing its solubility.^{22,23} Although the influence of HBDs hydroxyl groups on DES interactions
205 with lignin has not been extensively studied, it was pointed out as one the factors favoring the
206 lignin extraction from biomass, such as oil palm empty fruit bunch.²⁴

207



208

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

213

214 Regarding the carboxylic acid-based DES, the capacity of dissolving Kraft lignin follows this order:
 215 [Ch]Cl:MaleA > [Ch]Cl:MalOA > [Ch]Cl:LacA > [Ch]Cl:MaliA > [Ch]Cl:OxaA. The best carboxylic
 216 acid-based DES was [Ch]Cl:MaleA by attaining 34.97 ± 0.33 wt% lignin solubility at 313.15 K.
 217 When contrasting the lignin solubility in [Ch]Cl:OxaA (C2), [Ch]Cl:MalOA (C3) and [Ch]Cl:MaleA
 218 (C4), the increasing number of carbons in the carboxylic acid structure favored lignin
 219 dissolution,²⁵ which is a similar finding to that observed for alcohol-based DES. Nevertheless,
 220 when comparing alcohol-based HBDs and carboxylic acid-based HBDs with equal chain length
 221 (C3 and C4), lignin solubility seems to be favored with carboxylic acids to the detriment of
 222 hydroxyl groups. An exception was observed between the smallest size HBDs, EGLY and OxaA,
 223 both structured by two carbons. Furthermore, an opposite behavior to alcohol-based DES was
 224 also observed with the additional hydroxyl group in MaliA reducing its ability for lignin

225 dissolution in contrast to its counterpart MaleA. In case of MaliA structure, the additional
226 hydroxyl group may increase the steric hindrance between HBD and lignin interaction, an
227 opposite behavior of the extra hydroxyl group in GLY structure discussed above. Regarding
228 MaleA, its double bond may contribute positively to the solvent interaction with lignin through
229 π - π interactions.^{24,26,27}

230 For both DES families studied in this work, a high capacity to solubilize Kraft lignin was always
231 achieved (>20 wt% lignin solubility). For instance, [Ch]Cl:HEXA and [Ch]Cl:MaleA led to an
232 increment in lignin solubility of around 1.16-fold and 1.23-fold in contrast to one of the most
233 broadly used DES, [Ch]Cl:LacA, respectively. The enhanced lignin solubility in DES is much more
234 evident when compared with pure water: 226-fold and 239-fold for [Ch]Cl:HEXA and
235 [Ch]Cl:MaleA, correspondingly. In other study, Soares et al²⁰ have also verified the great ability
236 of several DES to enhance the solubility of Kraft lignin. In their work, a different type of DES that
237 maximized lignin solubility was found, namely urea:propionic acid (U:PA), which allowed 359-
238 fold higher Kraft lignin solubility than water.

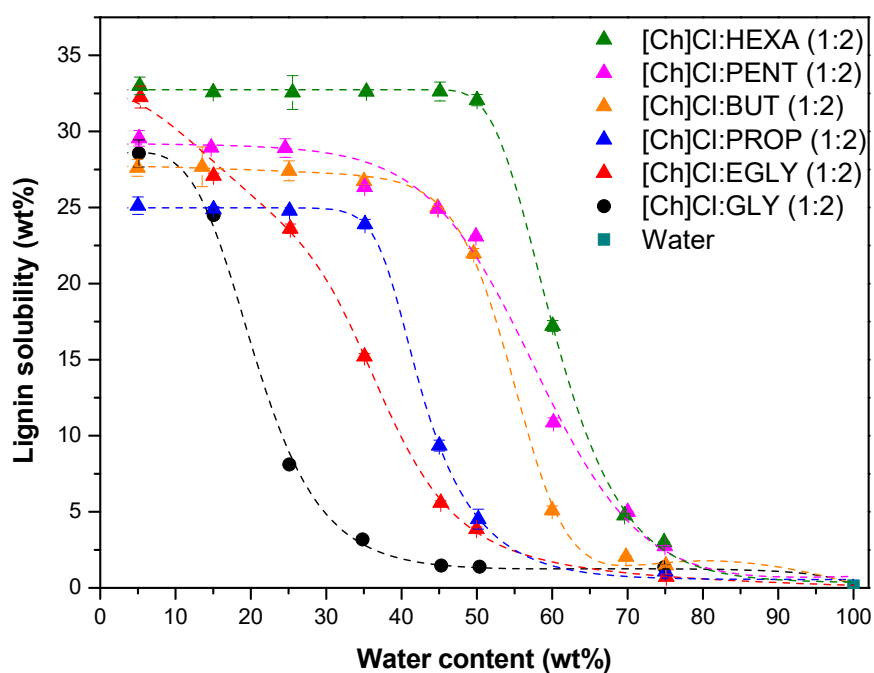
239 Thus far, the disclosed data suggest that functional groups in HBD constituent substantially
240 affect the ability of DES for Kraft lignin dissolution, demonstrating the importance of selecting a
241 suitable combination of HBA:HBD for such purpose.

242

243 **The effect of water content on Kraft lignin dissolution.** The influence of water concentration (5
244 wt% to 100 wt% content) on the ability of DES to dissolve lignin was also addressed. The
245 solubility of Kraft lignin in both alcohol-based DES aqueous solutions and carboxylic acid-based
246 DES aqueous solutions at 313.15 K are shown in Figure 2 and Figure 3, respectively.

247 The obtained data with alcohol-based DES systems demonstrated high dependency on water
248 content. The addition of water negatively affected the ability of those DES to dissolve lignin and
249 depending on the alcohols chemical structure different solubility behaviors were observed.²⁸ For
250 instance, at 5 wt% water content, [Ch]Cl:EGLY was the second best DES for lignin dissolution

251 among studied solvents, but the addition of 25 wt% water turn this DES the second worst. The
 252 negative impact of water was more pronounced for [Ch]Cl:GLY, which enabled only 8.11 wt%
 253 lignin solubility at 25 wt% water content. This represents a decrease of more than 70 % on the
 254 ability of [Ch]Cl:GLY (at 5 wt% water content) to dissolve Kraft lignin. The additional hydroxyl
 255 group in the GLY's chemical structure in comparison to other HBDs might explain this drastic
 256 reduction of lignin solubility in presence of water. In alcohols-based DES, the hydroxyl groups in
 257 HBD's structure governs hydrogen bond interactions with Kraft lignin functional groups enabling
 258 its dissolution in DES. However, water molecules will compete for those interactions hindering
 259 the capacity of those DES to promote hydrogen bonding network with lignin.²⁹⁻³¹ Since GLY
 260 comprises three hydroxyl groups in its structure, the impact of water is larger than for other
 261 HBDs with only two hydroxyl groups, such as EGly.²²



262
 263 **Figure 2.** The influence of water content on the solubility of Kraft Lignin in alcohol-based DES at
 264 323.15 K. All examined DES were tested with the HBA:HBD molar ratio of 1:2 .Dashed lines are
 265 visual guides.

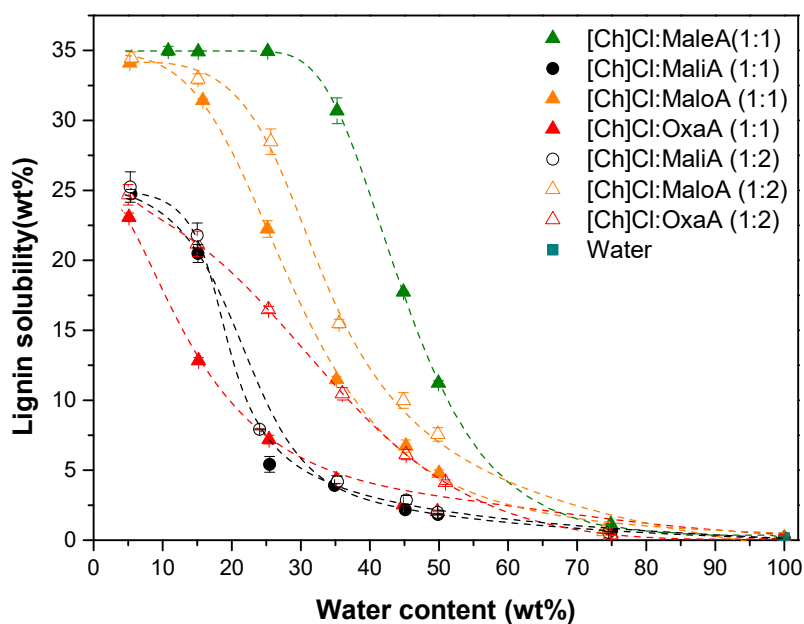
266

267 On the other hand, the negative impact of water was less pronounced for [Ch]Cl:PROP,
268 [Ch]Cl:BUT, [Ch]Cl:PENT, and [Ch]Cl:HEXA. In fact, at low water contents the influence of water
269 is low or negligible on the performance of those DES allowing a plateau on lignin solubility values
270 (Figure 2). For example, [Ch]Cl:PROP presented a stable lignin solubility up to 35 wt% water
271 content. The increase of HBD's carbon chain length enabled a higher stability in lignin solubility
272 for higher water contents as observed in the case of [Ch]Cl:HEXA, which maintained lignin
273 solubility near 33 wt% up to approximately 55 wt% water content. Similar observations were
274 reported by Soares et al.^{20,21} and Cláudio et al.³² when using DES and ILs capable of enhancing
275 the solubility of phenolic compounds in aqueous media.

276 From the obtained lignin solubility curves, it can be inferred that dispersive interactions
277 promoted by HBD's alkyl chains seem to be important to dissolve lignin and to maintain its
278 solubility in aqueous media. However, how do those dispersive forces influence the lignin
279 dissolution process? The sigmoidal shape of the solubility curves using [Ch]Cl:PROP, [Ch]Cl:BUT,
280 [Ch]Cl:PENT and [Ch]Cl:HEXA aqueous solutions suggests that the solubility of Kraft lignin in
281 these systems is driven by a hydrotropic mechanism.^{33,34} Those DES, and specially the HBD, self-
282 organizes around lignin macromolecules in presence of water maintaining its solubility. This self-
283 organization is improved with the higher length of HBD's carbon chain as consequence of
284 stronger dispersive forces between the alkyl chains.

285 In order to confirm this dissolution mechanism, the Kraft lignin solubility curves of those DES
286 aqueous solutions were fitted using the Shimizu and Matubayasi hydrotropy model³⁴ (Figures
287 S3 and S4 in supporting information). The experimental data could be well described by the
288 model, showing a cooperative hydrotropy as defined by Shimizu and Matubayasi.³⁴ The
289 sigmoidal profile of the obtained lignin solubility curves suggests a cooperative intermolecular
290 interaction involving hydrotrope molecules participating in the dissolution process as reported
291 by Balasubramanian et al.³⁵

292 A similar effect of water was found in Kraft lignin solubility with carboxylic acid-based DES
 293 aqueous solutions (Figure 3). For instance, the lignin dissolution performance of [Ch]Cl:MaleA
 294 was not affected by low water contents (up to 25 wt%), which might be related to the alkyl chain
 295 length of MaleA (C4). As discussed above, increasing the alkyl chain length of the HBD may favor
 296 lignin dissolution in DES. On the other hand, the presence of an extra hydroxyl group in C4 alkyl
 297 chain length of MaliA had a direct impact on the drastic drop of lignin solubility in [Ch]Cl:MaliA
 298 at same water content range. Besides the steric hindrance discussed above, the existence of an
 299 extra hydroxyl group capable of competing for hydrogen bonds with water molecules does not
 300 favor lignin dissolution in aqueous media.^{36,37} For other studied carboxylic acid-based DES,
 301 abrupt decreasing trends in Kraft lignin solubility was also observed in presence of water, which
 302 represents a co-solvency behavior of those DES.²¹
 303



304
 305 **Figure 3.** The influence of water content on the solubility of Kraft Lignin in carboxylic acid-based
 306 DES at 323.15 K. All examined DES were tested with the HBA:HBD molar ratio of 1:1 and 1:2.
 307 Exceptionally, since a clear liquid is not formed with [Ch]Cl:MaleA (1:2), no lignin solubility data
 308 was obtained for this system. Dashed lines are visual guides.

309

310 The data depicted in Figures 2 and 3 also demonstrates that the negative effect of water on Kraft
311 lignin solubility is more pronounced in carboxylic acid-based DES than their alcohol counterparts
312 at high water contents. In some cases, the lignin solubility is low or negligible at high water
313 concentrations, showing the anti-solvent character of water. Chen et al.³⁸ reported that the
314 presence of large amounts of water impairs the lignin dissolution capacity of the DES, since
315 water molecules compete for hydrogen bonds with the solvent.

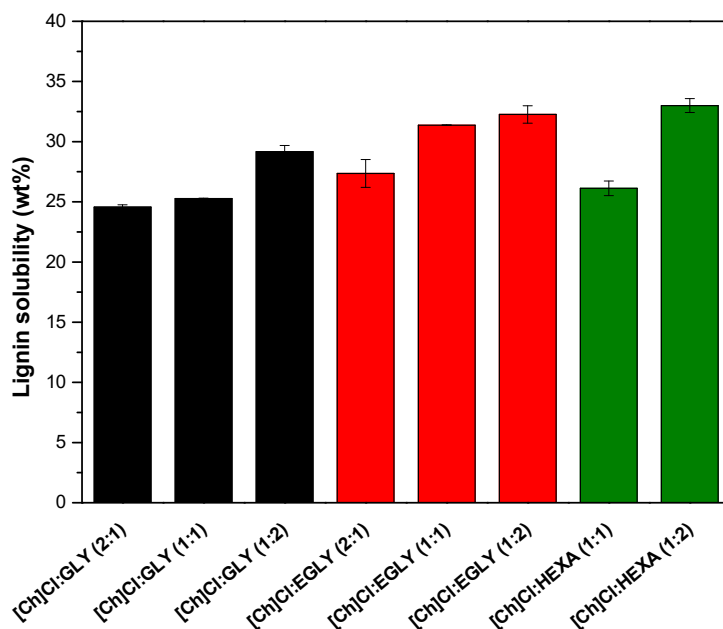
316

317 **The effect of HBA:HBD molar ratio on Kraft lignin dissolution.** The molar ratio between HBA
318 and HBD in DES composition directly impacts its physicochemical properties, including the
319 solvent power for a specific solute. Therefore, the influence of the HBA:HBD molar ratio on Kraft
320 lignin solubility was also studied in this work. Three alcohol-based DES ([Ch]Cl:GLY, [Ch]Cl:EGLY,
321 [Ch]Cl:HEXA) and four carboxylic acid-based DES ([Ch]Cl:OxaA, [Ch]Cl:MaloA, [Ch]Cl:MaleA,
322 [Ch]Cl:LacA) with different molar ratios were tested for Kraft lignin solubility at 313.15 K.
323 According to the results presented in Figure 4 and Figure 5, the HBA:HBD molar ratio influenced
324 Kraft lignin solubility.

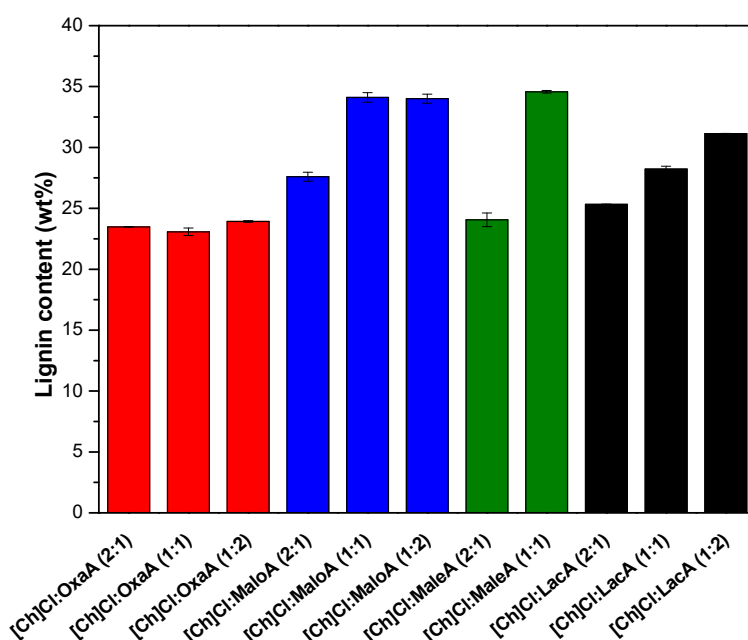
325 Contrasting the lignin solubility in alcohol-based DES, the highest solubility enhancement was
326 observed for [Ch]Cl:HEXA (1:2) to around 0.26-fold higher than [Ch]Cl:HEXA (1:1) (Figure 4).
327 Similar observation was found when using the various HBA:HBD molar ratios studied for
328 [Ch]Cl:GLY and [Ch]Cl:EGLY. Analogously, the increase of HBD content in [Ch]Cl:MaleA enabled
329 40 % higher lignin solubility for (2:1) ratio when compared to (1:1) (Figure 5). On the other hand,
330 the lignin solubility enhancement was practically negligible when increasing OxaA content.

331 In both cases, alcohol- or carboxylic acid-based DES, a higher HBD molar ratio enhanced lignin
332 solubility. This clearly suggests that HBD exhibit a crucial role on Kraft lignin dissolution in DES
333 to the detriment of HBA. Francisco et al.¹⁶ also observed that lignin solubility decreases with
334 increasing amounts of [Ch]Cl (HBA). Moreover, the dispersive interactions favored by long alkyl

335 chain lengths of the HBD (e.g. HEXA and MaleA) favors this solubility improvement rather than
 336 short alkyl chain lengths (EGly and OxaA). This was also highlighted in another study showing
 337 the ability of DES to dissolve lignin model compounds.²⁰



338
 339 **Figure 4.** The influence of HBA:HBD molar ratio on the solubility of Kraft lignin in alcohol-based
 340 DES at 313.15 K. All examined DES were tested at 5 wt% water content. A liquid mixture of
 341 [Ch]Cl:HEXA (2:1) was not successfully achieved at 313.15 K.



342

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

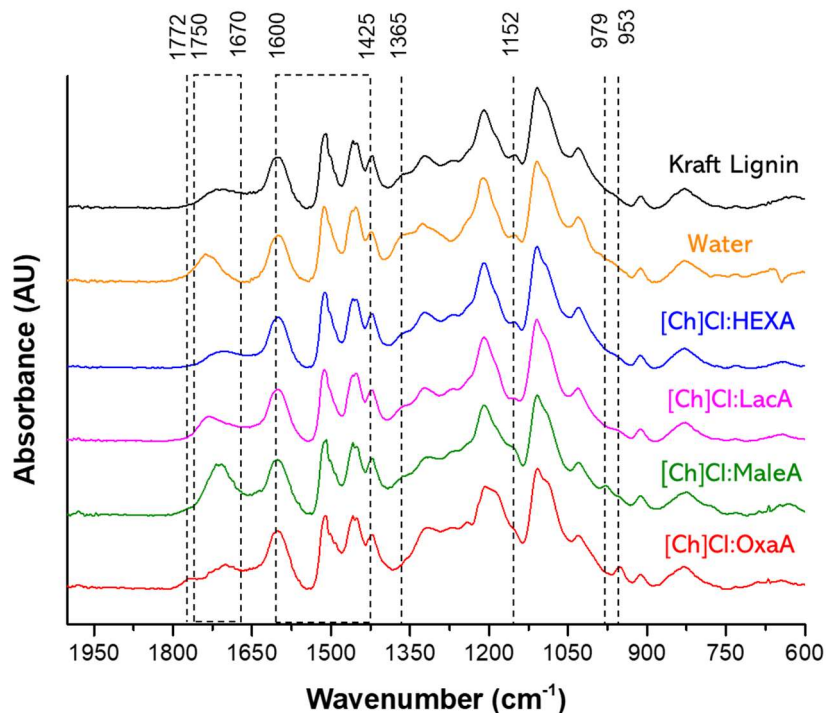
346

347 **Structural changes of Kraft lignin after thermal treatment with DES.** The second part of this
348 work addressed the potential of DES to valorize Kraft lignin. Kraft lignin was submitted to
349 thermal treatment assisted by DES at 393.15 K for 6 hours and was followed by a comprehensive
350 characterization of the regenerated lignin (precipitated with water), including spectroscopic,
351 thermal and elemental analysis. Those conditions were chosen to simulate lignin
352 depolymerization processes usually applied in literature.³⁹⁻⁴¹ Four of the above studied DES,
353 namely [Ch]Cl:HEXA (1:2), [Ch]Cl:MaleA (1:1), [Ch]Cl:OxaA (1:1) and [Ch]Cl:LacA (1:1) were used
354 for these experimental trials. [Ch]Cl:HEXA (1:2) and [Ch]Cl:MaleA (1:1) were selected due to their
355 highest solubility performances for Kraft lignin, while the interest in studying [Ch]Cl:OxaA (1:1)
356 relied on its high acidity. [Ch]Cl:LacA, which has been largely used in biomass delignification
357 processes reported in literature,^{11,42,43} was chosen as reference.

358

359 *FTIR-ATR analysis.* The impact of selected DES on Kraft lignin structure was first evaluated by
360 FTIR analysis. The band assignments were performed according to lignin infrared
361 characterization reported in literature.⁴⁴⁻⁴⁸ The list of lignin vibrational bands/regions and
362 corresponding assignments are presented in detail in the supporting information (Table S3)
363 along with full spectra (Figure S4). For comparison, the spectra were organized from Kraft Lignin
364 at the top to the most modified lignin spectrum at the bottom (Figure 6).

365



366

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

370

371 At first sight, all infrared spectra show a typical Kraft lignin fingerprint as observed in the region
 372 1750-750 cm^{-1} disclosed in Figure 6. Characteristic Kraft lignin absorption bands with notable
 373 high intensities at 838, 1109, 1212, 1327, 1456, 1514, 1600 cm^{-1} were observed in all spectra,
 374 suggesting limited changes in the Kraft lignin chemical structure after thermal treatments. The
 375 lignin recovered from water treatment presented similar spectrum to that of Kraft lignin,
 376 showing the ineffective action of water to change lignin structure at studied conditions. Amongst
 377 examined DES, [Ch]Cl:HEXA exhibited a non-derivatizing behavior for Kraft lignin, since the same
 378 characteristic vibrational bands were observed for its recovered lignin and no additional band
 379 was detected.

380 On the other hand, carboxylic acid-based DES demonstrated evidences of lignin chemical
 381 modification. For example, [Ch]Cl:LacA-lignin spectrum presented a band shift from 1700 to

382 1736 cm^{-1} and simultaneous intensity decrease of the band at 1152 cm^{-1} . The presence of the
383 band at 1736 cm^{-1} could be associated to C=O stretching in ester groups formed by esterification
384 of lactic acid molecules with lignin hydroxyl groups. This side reaction has been also shown in
385 thermal treatments of lignin model compounds with [Ch]Cl:LacA.⁴⁹ The decreasing intensity of
386 the band at 1152 cm^{-1} , which is assigned to C–O–C vibration in polysaccharides, indicates the
387 removal of residual contents of hemicelluloses and cellulose as consequence of their acid
388 hydrolysis mediated by the carboxylic acid. Similar trends can be also observed in FTIR spectra
389 of recovered lignins from the more acidic [Ch]Cl:OxaA and [Ch]Cl:MaleA treatments. Moreover,
390 additional bands at 953 and 979 cm^{-1} were observed in [Ch]Cl:OxaA-lignin and [Ch]Cl:MaleA-
391 lignin spectra, respectively, suggesting possible variations of lignin chemical structure or
392 contamination of [Ch]Cl:OxaA and [Ch]Cl:MaleA.

393

394 *Elemental analysis.* The results obtained from the elemental analysis (Table 2) of and recovered
395 lignins showed a minimal impact of the thermal treatments on carbon, hydrogen and oxygen
396 contents. Although at much less content, a sharp variation of nitrogen in lignins recovered from
397 thermal treatments with carboxylic-based DES was observed. This is mostly pronounced in
398 [Ch]Cl:MaleA-lignin and [Ch]Cl:OxaA-lignin samples, in which the nitrogen content increased
399 almost 2.6- and 4.7-fold the original content in Kraft lignin. These results indicate a
400 contamination of [Ch]Cl in those lignin samples, supporting the conclusions inferred from the
401 FTIR data. On the other hand, the sulfur content in lignin samples followed an opposite trend.
402 The 2 wt% sulfur content in Kraft lignin was substantially reduced with thermal treatments,
403 especially with carboxylic-acid DES. For instance, the treatments with [Ch]Cl:MaleA and
404 [Ch]Cl:OxaA allowed a sulfur content reduction to almost half of the original. It should be
405 emphasized that sulfur content is one the major deterrents of Kraft lignin valorization, thus its
406 removal is beneficial.^{50,51}

407

408 **Table 2.** Elemental characterization of Kraft lignin and recovered lignins from thermal
 409 treatments (393.15 K for 6 h) with water, [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1)
 410 and [Ch]Cl:OxaA (1:1). All examined DES were tested at 5 wt% water content. The data is
 411 expressed as means and corresponding standard deviations.

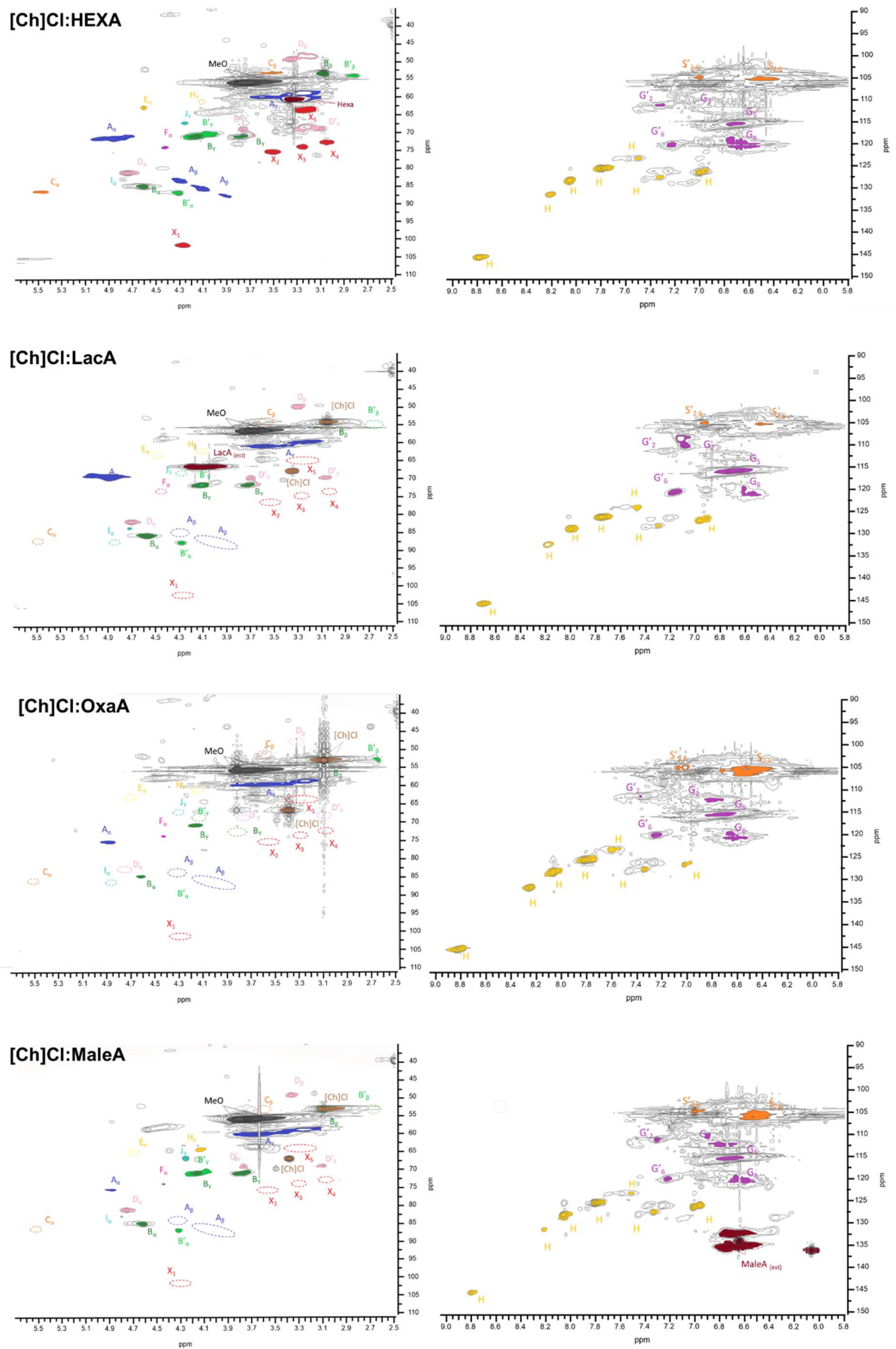
Samples	Elemental Analysis (wt%)				
	C	H	N	S	O
Kraft lignin	60.71±0.29	5.35±0.03	0.14±0.01	2.00±0.15	30.37±0.28
Water-lignin	63.03±0.13	5.55±0.02	0.13±0.00	1.47±0.01	28.22±0.26
[Ch]Cl:HEXA-lignin	63.38±0.00	5.66±0.07	0.15±0.01	1.46±0.26	28.47±0.40
[Ch]Cl:LacA-lignin	63.58±0.09	5.34±0.09	0.24±0.00	1.33±0.03	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

412

413 *2D HQSC NMR analysis.* The structural analysis of lignin samples was complemented with the 2D
 414 HQSC NMR technique to better understand the impact of thermal treatments with DES. The
 415 HSQC oxygenated and aromatic regions of the Kraft lignin along with the representation of
 416 identified lignin subunits are shown in supplementary information (Figure S5 in SI) to suitably
 417 address its chemical characterization. The ¹³C-¹H cross signal assignments are also described in
 418 supporting material (Table S4 in SI) according to data reported in literature.⁵²⁻⁵⁸

419 The HSQC analysis of recovered lignin samples from thermal treatments with [Ch]Cl:HEXA,
 420 [Ch]Cl:LacA, [Ch]Cl:MaleA and [Ch]Cl:OxaA revealed different behaviors between these DES
 421 regarding their capacity to modify lignin structure. The HSQC spectra of recovered lignins after
 422 thermal treatment with those DES are depicted in Figure 7.

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



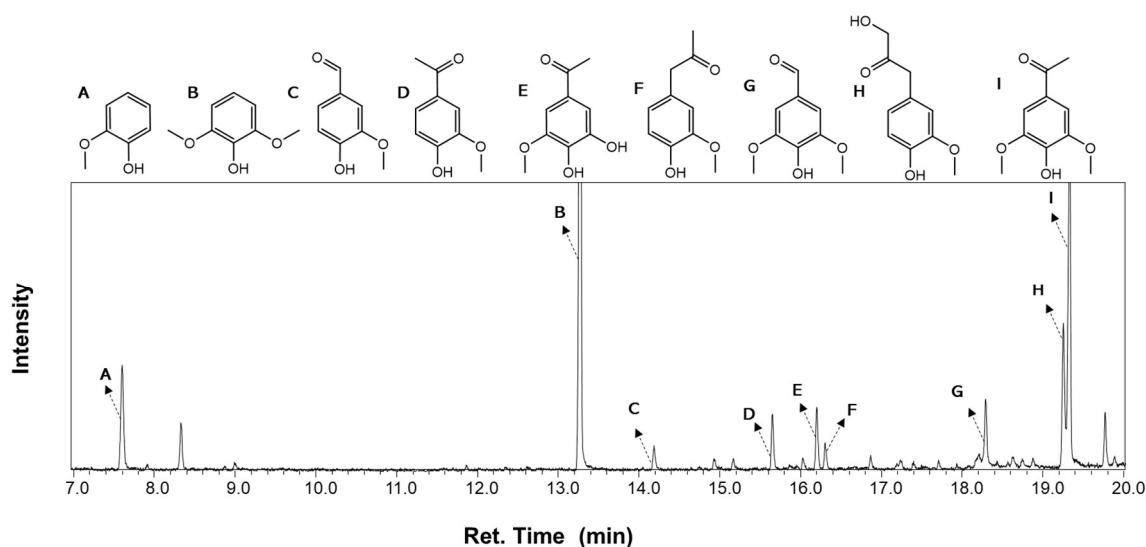
428 **Figure 7.** 2D HSQC NMR of recovered lignins from thermal treatments (393.15 K for 6 h) with

429 [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1) and [Ch]Cl:OxaA (1:1). All examined DES
430 were tested at 5 wt% water content. The corresponding ^{13}C - ^1H cross signals of main lignin
431 substructures are assigned, while resonances related to DES contamination were also
432 attributed.

433

434 On the other hand, carboxylic-based DES enabled the disruption of important lignin chemical
435 bonds, specially C-O covalent bonds, whereas different levels of structural modification were
436 observed. The HSQC spectra of recovered lignins demonstrated an increased reactivity of
437 examined DES in the following order: [Ch]Cl:LacA < [Ch]Cl:MaleA < [Ch]Cl:OxaA. In all cases, an
438 absence of C_{β} - H_{β} correlations of the alkyl-aryl ether structures (A) at 83.96/4.31 ppm (guaiacyl
439 type) and 87.23/3.69 ppm (syringyl type) was observed. On the other hand, the cross signals
440 from α (81.36/4.78 ppm) and γ (59.0/3.2 and 59.9/3.7 ppm) positions in the same substructure
441 were maintained, although depicting different intensities among spectra. These results suggest
442 that the acidity provided by these carboxylic-based DES allowed the cleavage of β -O-4 bonds in
443 lignin macromolecules. Furthermore, all signals related to phenylcoumaran substructures (C)
444 vanished, representing the cleavage of α -O-4 chemical linkages in lignin. On the other hand,
445 other relevant lignin substructures, including pinoresinol (B) and spirodienone (D), were
446 maintained in Kraft lignin treated with [Ch]Cl:LacA and [Ch]Cl:MaleA. This was not observed for
447 [Ch]Cl:OxaA-lignin spectrum, in which the cross signals from the spirodienone substructure (D)
448 were not visible. It possibly indicates the higher capacity of oxalic acid for the cleavage of α -O- α
449 linkages, which could be associated to its higher acidity ($\text{pka}_{1(\text{OxaA})} = 1.42$) than their acid
450 counterparts ($\text{pka}_{1(\text{MaleA})} = 1.94$; $\text{pka}_{1(\text{LacA})} = 3.86$). Unsurprisingly, the cross signals related to xylan
451 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
452 ppm (X_2) and 101.80/4.29 ppm (X_1) disappeared in all cases, indicating the removal of residual
453 xylan present in Kraft lignin through acid hydrolysis of the carbohydrate glycosidic linkage
454 mediated by carboxylic acid-based DES.

455 To confirm the high reactivity of [Ch]Cl:OxaA, a standard GC/MS analysis of the liquid phase
 456 obtained after Kraft lignin thermal treatment with this DES was performed. The acquired GC
 457 chromatogram (Figure 8) depicted the existence of several lignin monomers, either S or G type
 458 unit, in the liquid phase after the thermal treatment. A total of 9 meaningful aromatic
 459 compounds were identified by contrasting with standard compounds and GC/MS databases. It
 460 is reasonable to mention that these compounds were formed by lignin depolymerization mostly
 461 through C-O cleavage assisted by [Ch]Cl:OxaA as mentioned above, but the obtained
 462 depolymerization profile also reveals possible C-C cleavage. For instance, guaiacol (A) and
 463 syringol (B) were detected and were probably formed from the cleavage of the aliphatic part of
 464 lignin phenylpropanoid units and/or other identified compounds (C to I in Figure 8).. Yet, more
 465 data is needed to elucidate this result. Overall, these results indicate that [Ch]Cl:OxaA can act as
 466 both solvent and catalytic agent resulting in partial lignin depolymerization and subsequent
 467 structural modification as shown by the HSCQ analysis.



468
 469 **Figure 8.** GC chromatogram of the liquid phase from Kraft lignin treatment with [Ch]Cl:OxaA
 470 (393.15 K–6h) showing the following aromatic compounds: (A) guaiacol, (B) syringol, (C) vanillin,
 471 (D) acetovanillone, (E) 3,4-dihydroxy-5-methoxyacetophenone, (F) guaiacylacetone, (G)
 472 syringaldehyde, (H) 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone and (I)
 473 acetosyringone.

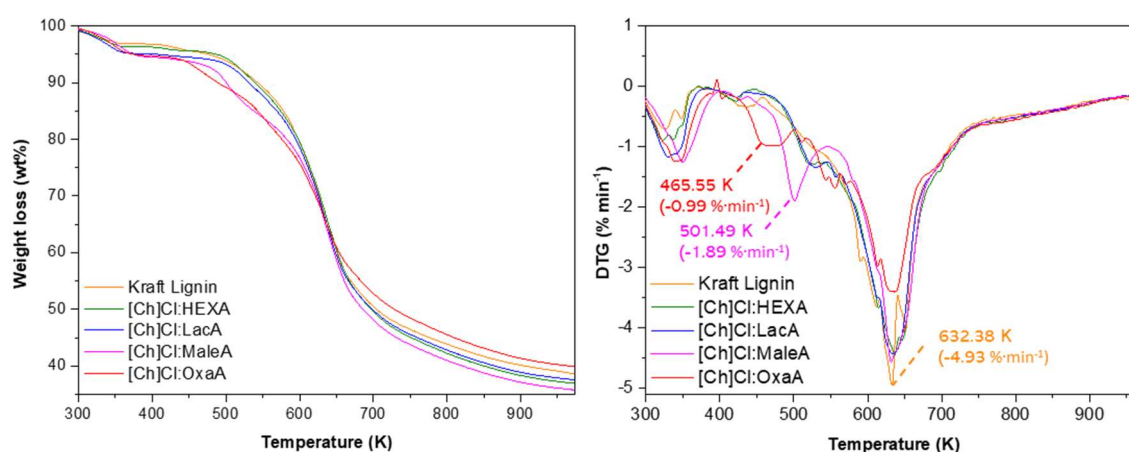
474

475 The HSQC data also revealed the presence of DES as contaminant in all treated lignins.
476 Resonances associated to [Ch] ion, such as CH₃ (54.50/3.30 ppm) and CH₂ (67.0/3.41 ppm)
477 groups were identified in spectra of recovered lignins from treatments with carboxylic-based
478 DES. This result is corroborated by the substantial increase in the amount of nitrogen in those
479 lignins found by elemental analysis as presented above (Table 2). The fact [Ch] is not present in
480 [Ch]Cl:HEXA-lignin spectrum suggests that a chemical binding between [Ch] and lignin might be
481 favored in acidic media. Alvarez-Vasco et al. also proposed a possible reaction between [Ch] and
482 lignin phenolic groups (lactic acid was used as HBD).¹¹ Furthermore, cross signals attributed to
483 carboxylic acids, such as lactic and maleic acids, were also found in HSQC spectra. Obviously,
484 carboxylic signals from oxalic acid are not seen in HSQC (lack of C-H coupling), but its presence
485 was confirmed by 1D NMR (data not shown). The esterification of these carboxylic acids with
486 lignin hydroxyl groups is most likely to occur as indicated by the intense C=O vibrational bands
487 in FTIR spectra previously reported (Figure 6).

488 A comparison between aromatic regions of HSQC spectra clearly shows that the aromatic
489 fractions of Kraft lignin are practically preserved, including S and G type units as well as p-
490 hydroxycinnamyl structures (H), after DES treatment. Although [Ch]Cl:OxaA demonstrated
491 ability for lignin depolymerization, the formation of depolymerized products from S and G type
492 units (Figure S7 in SI) indicates no selective cleavage.

493 The FTIR, elemental analysis and 2D NMR data elucidated the chemical modifications of Kraft
494 lignin in presence of alcohol- and acid-based DES. On the one hand, the non-derivatizing
495 behavior of alcohol-based DES, such as [Ch]Cl:HEXA, [allows their application as solvents for the](#)
496 [design of tailored reactions of lignin into new products](#). On the other hand, carboxylic acid-based
497 DES showed ability to depolymerize lignin in valuable monomeric compounds through ether
498 bond cleavage increasing the value of Kraft lignin, but part of the solvent seems to react with
499 the remaining non-depolymerized fraction by esterification. Although consumption of the

500 solvent would be seen as negative effect, in this case the integration of dissolution and
 501 functionalization of lignin with esterified carboxylic acids may be envisaged as an opportunity to
 502 increase the cost-efficiency in the production of new lignin bio-based composites and materials.
 503 For instance, lignin esters of maleic acid have been used for the improvement of lignin reactivity
 504 towards grafting reactions in thermal processes⁵⁹ as well as for the functionalization of lignin
 505 nanoparticles as plastic fillers.⁶⁰
 506
 507 *TGA analysis.* The thermal stability of Kraft lignin and DES-treated lignins was also addressed.
 508 Figure 9 shows the thermal decomposition curves and corresponding derivatives in the
 509 temperature range between 303.15 and 973.15 K.



510
 511 **Figure 9.** TGA (left) and DTGA (right) curves of Kraft lignin and recovered lignins from thermal
 512 treatments (393.15 K for 6 h) with [Ch]Cl:HEXA (1:2), [Ch]Cl:LacA (1:1), [Ch]Cl:MaleA (1:1) and
 513 [Ch]Cl:OxaA (1:1). All examined DES were tested at 5 wt% water content.

514
 515 The TGA data demonstrated that treated lignins exhibited similar thermal profiles to that of Kraft
 516 Lignin. Yet, relevant differences can be highlighted. Among examined samples, [Ch]Cl:MaleA-
 517 lignin and [Ch]Cl:OxaA-lignin showed the highest mass loss between 350 and 600 K. However,
 518 after this temperature range, [Ch]Cl:OxaA-lignin demonstrated higher thermal stability (60.1
 519 wt% loss) than others (62.5-64.2 wt% loss), including Kraft lignin (61.4 wt% loss) as depicted in

520 Figure 8. The higher thermal stability of [Ch]Cl:OxaA-lignin can be correlated to its composition
521 of recalcitrant structures, such as pinoresinol containing β - β linkages, to the detriment of more
522 susceptible structures for cleavage (*e.g.* aryl ether) as depicted in HSQC spectra. Furthermore,
523 the high reactivity of [Ch]Cl:OxaA not only favors the cleavage of aryl ether structures, but also
524 may enable the formation of lignin condensed fractions difficult to pyrolyze. After ether bond
525 cleavage, radical couplings could be formed, which in turn establish intricate inter/intra C-O and
526 inter-C-C bonds that require high dissociation energies.⁶¹

527 On the other hand, the highest mass loss of lignins treated with [Ch]Cl:OxaA-lignin and
528 [Ch]Cl:MaleA at 350-600 K range mentioned above is clearly expressed in DTGA curves with
529 peaks of weight loss rate at 465.55 K and 501.49 K, respectively (Figure 8). Contrasting to
530 literature data, these mass losses are most likely to be representative of oxalic and malic acid
531 contaminations.^{62,63} This reflects the identified contaminations observed before in NMR
532 analysis. Moreover, the maximum DTG values (DTG_{max}) were detected between 625 and 640 K
533 for all lignin samples. This mass loss is related to the fragmentation of lignin interunit bonds⁶⁴
534 and seems to be quite similar between almost all lignin samples with no grid differences when
535 compared to Kraft lignin. An exception can be observed for [Ch]Cl:OxaA-lignin (Figure 8), which
536 follows a different pattern represented by a lower weight loss rate and a slight DTG_{max} deviation.
537 This can be associated to lignin chemical changes induced by [Ch]Cl:OxaA as explained before.

538

539 **CONCLUSIONS**

540 The present work demonstrated the ability of DES to dissolve Kraft lignin and their potential to
541 chemically modify this underrated by-product of pulp and paper industries.

542 The obtained results showed that DES HBD play an important role in Kraft lignin dissolution and
543 their efficiency is governed by its chemical nature (alcohol or carboxylic), chain length and molar
544 ratio to HBA. Furthermore, the addition of water negatively affects the lignin solvation power of

545 DES. Among the examined DES, [Ch]Cl:HEXA and [Ch]Cl:MaleA showed the best performance for
546 Kraft lignin dissolution, allowing 32.99 and 34.97 wt% wt% solubility at 313.15 K, respectively.
547 Besides, the thermal treatments (393 K) of Kraft lignin with selected DES demonstrated that
548 carboxylic acid-based DES induce chemical modifications to Kraft lignin, especially the disruption
549 of C-O covalent bonds (*e.g.* β -O-4, α -O-4 and α -O- α). Furthermore, the acidity power of
550 carboxylic acid-based DES has a direct impact on the chemical modification of Kraft lignin, while
551 alcohol-based DES were found to be excellent non-derivatizing solvents by maintaining the lignin
552 chemical structure.
553 The results shown in this work highlight the versatility of these solvents, which depending on
554 their chemical structure and composition may offer a different lignin valorization pathways: i)
555 partial lignin depolymerization with carboxylic acid-based DES into added value low molecular
556 weight compounds and simultaneous esterification of the non-depolymerized fraction as
557 precursor to new product formulations; or ii) dissolution of underivatized lignin for target
558 modifications using alcohol-based DES towards new bio-based materials.

559

560 **Supporting information**

561 List of compounds used in this work; Kraft lignin calibration curve; Kraft Lignin solubility data;
562 description of Shimizu and Matubayasi hydrotrophy model and correlation with solubility data;
563 Lignin characterization: spectra and assignments of FTIR-ATR and 2D HSQC; GC-MS methodology
564 and GC chromatogram of depolymerized fraction of [Ch]Cl:OxaA-lignin;

565

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575

576 **Abbreviations**

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

581

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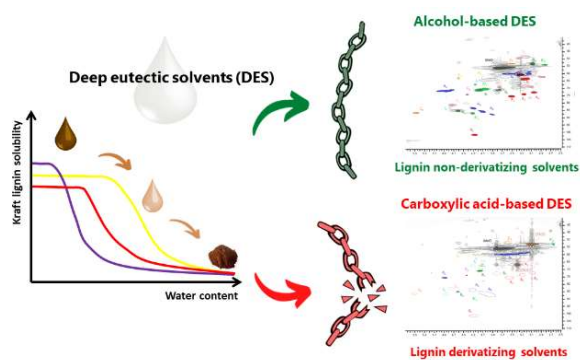
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803 TOC/Abstract Graphic



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806 **Synopsis.** A comprehensive study showing that depending on the chemical nature of deep
807 eutectic solvents different valorization strategies for Kraft lignin can be accomplished.

808